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Analysis of thermoelectric materials for the direct conversion of nuclear energy

Glenn Earl Russcher

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FOR THE DIRECT CONVERSION OF NUCLEAR
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ANALYSIS OF THERMOELECTRIC MATERIALS
FOR THE DIRECT CONVERSION OF NUCLEAR ENERGY

by

Glenn Earl Russcher

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Nuclear Engineering

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1964

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INTRODUCTION

Nuclear energy offers unique solutions to several current power problems. Central station power plants, remote region power sources, mobile power supplies, and space mission power sources have all been considered as potential nuclear energy fields.

The success of nuclear energy must be founded on the capacity to produce power in a manner which is superior to a competitive technique. For example, as the source of central station power, cost per unit electrical power must be comparable to that for fossil fueled steam turbogeneration. As a mobile or remote region source it must provide reliable, maintenance free, logistic free service for extended periods. Power sources used in space require long life and reliability in addition to the highest possible energy to weight ratio.

It is proposed here that the direct conversion of nuclear energy to electricity may be fundamental to a better solution to some of these problems. Thermoelectricity is considered here as one approach. Its technology is more reliably developed than either of the other two major direct conversion techniques, thermionics or magnetohydrodynamics. Specifically, the state of the art has advanced to the point where laboratory scale thermoelectric systems are

being tested.

The development of thermoelectric direct conversion has been encouraged and supported in significant measure by the Federal Government through the Atomic Energy Commission and the Department of Defense. The major emphasis in this development has been the construction of devices using existing materials and the state of the art to demonstrate feasibility.

Feasibility has been successfully demonstrated; however, the efficiency of the conversion of thermal energy to electricity has been only a few per cent at best. Other than for specialized military applications, thermoelectric direct conversion would not appear to be a desirable partnership for nuclear energy. Radioisotope thermoelectric devices have successfully provided relatively small power requirements, less than 1 kw. The area best served by nuclear reactor thermoelectric conversion systems is that of power requirements greater than 1 kw where thermoelectric conversion must also compete with the two phase mercury turbogenerator conversion system.

Thermoelectric direct conversion has several inherent advantages, the most obvious being that no moving parts are involved, hence no maintenance is required during the device's lifetime. In addition, with the use of all solid materials, a system may be designed which is quite resistant to shock or vibration loading, two very restrictive design

criteria for space vehicle systems.

The major problem associated with thermoelectricity is the efficiency of the conversion. The question arises as to whether low efficiency is an innate property of thermoelectrics, and if not, how may it be improved. Specifically, how can the use of thermoelectrics, both existing and predicted, be best utilized for the optimum conversion of nuclear energy to electrical energy?

An analysis of the problems associated with the thermoelectric direct conversion of nuclear energy to electricity is begun with a literature survey of thermoelectricity.

LITERATURE SURVEY OF THERMOELECTRICITY

The conventional flows of heat and electricity in a material and the potentials producing them are nonreversible processes. A classic example of this fact is the production of electrical resistance heat at the rate $Q = I^2R$, regardless of the direction of flow of the electricity; however, it is impossible to generate a current I in the conductor simply by supplying the heat Q to the resistance volume R . In contrast, however, are the reversible processes known as the Seebeck effect, the Peltier effect and the Thomson effect.

The Seebeck effect which was discovered in 1823 by T. J. Seebeck results in an emf in a circuit composed of two different homogeneous materials if the junctions of the materials are at different temperatures. For small temperature differences, the emf depends on the temperature difference and is a function of the material used. The Seebeck coefficient between the materials A and B is S_{AB} and both E_{AB} and S_{AB} are positive if conventional current flow is from A to B at the hot junction.

$$E_{AB} = S_{AB} \Delta T = (S_A - S_B) \Delta T \quad 1$$

Actually the Seebeck coefficient of a pair of materials is the difference of their absolute coefficients.

The Peltier effect was discovered in 1832 by J. C. A. Peltier. Whenever a circuit composed of two dissimilar

materials carries an electric current, heat is absorbed at one junction and released at the other at a rate that is proportional to the current. This is called the Peltier effect, and the heat transferred is called the Peltier heat. Resistance heating is of course nonreversible and proportional to the square of the current. The Peltier coefficient, π_{AB} , is positive if current flow is from A to B at the junction where heat is absorbed, and the coefficient is really the difference of the absolute coefficients as in the Seebeck effect.

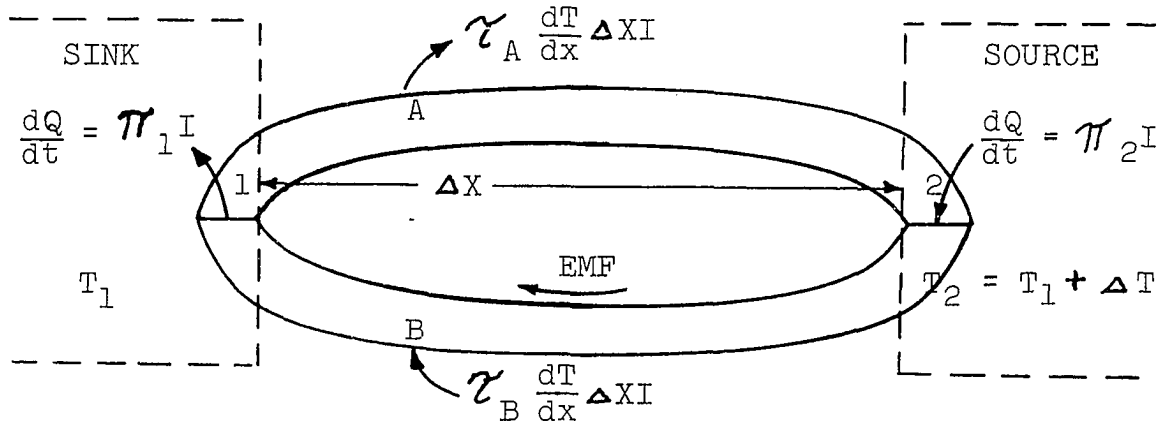
$$\frac{dQ_{AB}}{dt} = \pi_{AB}I = (\pi_A - \pi_B)I \quad 2$$

W. Thomson studied the Seebeck and Peltier effects, and derived a relation between their coefficients. He also predicted a new effect called the Thomson effect which is related to the reversible absorption or release of heat in a homogeneous conductor carrying a current through a temperature gradient. The rate of heat absorbed per unit length of conductor is equal to the positive coefficient times the conventional current and temperature gradient which are both in the same direction.

$$\frac{dQ_A}{dt} = \tau_A I \frac{dT}{dx} \quad 3$$

Thomson postulated that the first and second laws of thermodynamics could be applied to the reversible

thermoelectric processes alone, in the presence of the irreversible resistance heating and thermal conduction. The first law of thermodynamics requires that the work done by the Seebeck effect in conducting a unit charge around the two conductor circuit must be equal to the thermal energy absorbed from the system.



The Seebeck potential generated $EMF = S_{AB} \Delta T$

The energy required per unit charge is $E = EMF/I$

$$EMF = I \int_{T_2}^{T_1} \zeta_B dT - \pi_1 I - I \int_{T_1}^{T_2} -\zeta_A dT + \pi_2 I$$

$$E = \frac{EMF}{I} = \pi_2 - \pi_1 + \int_{T_2}^{T_1} (\zeta_B - \zeta_A) dT$$

4

$$\text{Let } \pi_1 - \pi_2 = \Delta\pi \quad \therefore \quad \Delta E = -\Delta\pi + (\zeta_B - \zeta_A) \Delta T$$

The second law requires that the total change in entropy of the system due to the passage of unit charge under reversible

conditions is zero.

$$0 = \frac{\pi_1}{T_1} + \frac{\pi_2}{T_2} + \int_{T_1}^{T_2} \frac{\tau_B - \tau_A}{T} dT \quad 5$$

Differentiating equations 4 and 5 with respect to temperature gives

$$S = \frac{dE}{dT} = \frac{d\pi}{dT} + \tau_B - \tau_A \quad 6$$

$$0 = \frac{d\pi}{dT} - \frac{\pi}{T} + \tau_B - \tau_A \quad 7$$

Subtract 7 from 6.

$$S = \frac{d\pi}{dT} - \frac{d\pi}{dT} + \frac{\pi}{T}$$

$$ST = \pi \quad 8$$

$$\text{Differentiating } \tau_A - \tau_B = T \frac{dS}{dT} \quad dS = (\tau_A - \tau_B) \frac{dT}{T}$$

$$S_A = \int_0^T \frac{\tau_A dT}{T} \quad d\pi = SdT + TdS \quad 9$$

$$\pi_A = TS_A \quad 10$$

These thermoelectric effects combine to provide useful power generation, heating or cooling. The efficient operation of such a thermoelectric circuit requires the optimization of the circuit and material parameters (18).

A thermoelectric cell is considered where the hot

junction is maintained at T_2 , the cold junction T_1 , and power is extracted from the cell. Under steady state conditions, the temperature gradient across the cell generates a Seebeck voltage $S_{12} \Delta T$ and its resultant current I . The heat balance is stated for the hot contacts T_2 . Q_a is the heat supplied to elements by the source, and Q_k that removed by conduction through the elements. Q_p is the Peltier heat removed by the current, and Q_j is the total Joule or resistance heating in the thermoelement arms. Effectively half of Q_j will appear at each junction. For a current I in the circuit, and neglecting Thomson heating.

$$Q_a + \frac{1}{2} Q_j = Q_k + Q_p$$

$$Q_p = \pi_{12} I = S_{12} I T_2$$

$$Q_j = I^2 (R_1 + R_2) = I^2 \left(\frac{\rho_1}{D_1} + \frac{\rho_2}{D_2} \right)$$

$$Q_k = (K_1 + K_2) \Delta T = (k_1 D_1 + k_2 D_2) \Delta T$$

$$Q_a = S_{12} I T_2 - \frac{I^2}{2} \left(\frac{\rho_1}{D_1} + \frac{\rho_2}{D_2} \right) + (k_1 D_1 + k_2 D_2) \Delta T \quad 11$$

For maximum power transfer to the load, the cell resistance $R_1 + R_2$ should be equal to the load resistance R_L . Under this condition, half the voltage $S_{12} \Delta T$ appears at R_L . The

$$\text{useful power is thus } P = \frac{(S_{12} \Delta T)^2}{4 R_L} . \quad 12$$

Similarly, the optimum current I_o that occurs at maximum power transfer follows.

$$I_o = \frac{S_{12} \Delta T}{R_L + R_1 + R_2} = \frac{S_{12} \Delta T}{2(R_1 + R_2)} \quad 13$$

Then to find the cell efficiency, η , at maximum power transfer, use equation 12 for the useful power, and equation 11 evaluated at the optimum current to find the heat energy required for this output. The electrical resistivity is ρ and thermal conductivity is k .

$$\eta = \frac{P_o}{Q_{a_o}} = \frac{\frac{S_{12}^2 \Delta T^2}{4R_L}}{\frac{S_{12}^2 \Delta T}{2R_L} T_2 - \frac{S_{12}^2 \Delta T^2}{8R_L^2} R_L + (k_1 D_1 + k_2 D_2) \Delta T} \quad 14$$

$$\eta = \frac{\Delta T}{2T_2 - \frac{\Delta T}{2} + 4 \frac{(k_1 D_1 + k_2 D_2)}{S_{12}^2} (R_1 + R_2)}$$

$$\eta = \frac{\Delta T}{2T_2 - \frac{\Delta T}{2} + 4 \frac{(K_1 + K_2)(R_1 + R_2)}{S_{12}^2}} \quad 15$$

For maximum efficiency, the parameters in the denominator of equation 15 must be a minimum. The last of these is $1/Z_{12}$ where Z_{12} is the figure of merit and is defined as

follows:

$$\begin{aligned}
 Z_{12} &= \frac{S_{12}^2}{(K_1 + K_2)(R_1 + R_2)} = \frac{S_{12}^2}{(k_1 D_1 + k_2 D_2) \left(\frac{\rho_1}{D_1} + \frac{\rho_2}{D_2} \right)} \\
 &= \frac{(k_1 D_1 + k_2 D_2) \left(\frac{\rho_1}{D_1} + \frac{\rho_2}{D_2} \right)}{(k_1 D_1 + k_2 D_2) \left(\frac{\rho_1}{D_1} + \frac{\rho_2}{D_2} \right)} \\
 &= k_1 \rho_1 + k_2 \rho_1 \frac{D_2}{D_1} + k_1 \rho_2 \frac{D_1}{D_2} + k_2 \rho_2 \\
 k_2 \rho_1 \frac{D_2}{D_1} &= k_1 \rho_2 \frac{D_1}{D_2} \quad \text{or} \quad \left(\frac{D_2}{D_1} \right)^2 = \frac{k_1 \rho_2}{k_2 \rho_1} \\
 k_1 \rho_1 + k_2 \rho_2 + 2k_1 \rho_2 \left(\frac{\rho_1 k_2}{\rho_2 k_1} \right)^{\frac{1}{2}} &= k_1 \rho_1 + k_2 \rho_2 + 2(k_1 \rho_2 k_2 \rho_1)^{\frac{1}{2}} \\
 &= \left[(k_1 \rho_1)^{\frac{1}{2}} + (k_2 \rho_2)^{\frac{1}{2}} \right]^2 \\
 \therefore Z_{12} &= \frac{S_{12}^2}{\left[(k_1 \rho_1)^{\frac{1}{2}} + (k_2 \rho_2)^{\frac{1}{2}} \right]^2}
 \end{aligned}$$

Thus for high efficiency and high figure of merit, the Seebeck coefficient should be high and the electrical resistivity and thermal conductivity should be low. These are not usually compatible conditions and since all are temperature dependent, the figure of merit may vary drastically from room temperature to some higher operating temperature.

These basic parameters are functions of the density of

the free charge carriers of the material. The Seebeck coefficient decreases as the charge carrier density increases, but both thermal and electrical conductivity increase with the increasing density. Actually it is only the electronic portion of the thermal conductivity which is affected; the lattice thermal conductivity is almost independent of any charge carrier effects.

The resultant effect on the figure of merit for a material due to a change in the charge carrier density has been shown by Ioffe (35) to be a pronounced maximum in the region where charge carrier density is between 10^{18} and 10^{21} carriers/cm³. Materials of this nature are referred to as highly doped semiconductors in the lower density region, and semimetals in the higher density region.

The charge carriers may be either electrons or holes, and may be introduced in many ways. Impurities may be added to a crystal, if the impurity atom has one more valence electron than the crystal lattice, the extra electron will be loosely bound in an energy level known as a donor level, possibly just below the conduction band. At room temperature this level may be raised into the conduction band, contributing to the charge carrier density. Similarly, an impurity atom which had one less valence electron than the lattice atoms would need one additional electron to satisfy its lattice valence bond, hence a hole or acceptor level is

introduced into the valence band. The movement of these holes or acceptors through the lattice constitutes a current of positive charge carriers.

These charge carriers may be introduced into a crystal lattice by vacancies and other defects as well as by impurity atoms. An atom which produces acceptor levels when it replaces a lattice atom may cause donor levels when trapped in the lattice as an interstitial. When the donor density is large, these energy levels spread out into a band called the impurity band which may provide electron conduction just as the conduction band does. Electron concentration may shift from one band to the other as temperature changes, thus the charge carrier density may or may not remain stable.

The only other physical property of thermoelectric materials which has been altered an amount significant enough to affect the figure of merit of the material is the thermal conductivity. Since the figure of merit increases with decreasing thermal conductivity, such an adjustment would be an important facet of the optimization of the figure of merit providing that it did not adversely effect the other physical properties. Ioffe (37) was the first to obtain a significant reduction in thermal conductivity by doping the thermoelectric material crystal lattice with a large amount of material whose atomic mass was very different, but whose electron structure was similar. This has become known as isoelectric

substitution. Since the wave length of phonons is of the same order of magnitude as the crystal lattice constants, any imperfection or distortion of the crystal lattice will impede or interfere with phonon flow. On the other hand, the wave lengths associated with the conduction electrons are many orders of magnitude larger than the crystal lattice constant, hence there is no change in the electrical conductivity. The net result is a marked increase in the thermoelectric efficiency. Williams (79) reports increases in the figure of merit by as much as 500% due to the isoelectric substitution of Si into Ge. The relation between 0 and 40 a/o Si was linear, with no break.

Thus it is apparent that to achieve a good thermoelectric material, low electrical resistivity but high thermal resistivity and Seebeck coefficient are desired. As the charge carrier density increases, electrical resistivity decreases, but thermal conductivity increases due to the electrical component and an adverse low thermal resistivity is approached. The product of these terms determines the desirable charge carrier density. Maximum conversion efficiency occurs near a charge carrier density of $10^{19}/\text{cm}^3$. Hence a search for thermoelectric materials must be directed at semiconductors or semimetals.

Since there are literally hundreds of compound semiconductors, it would be very desirable to be able to predict

the properties of a given material, without performing detailed experiments on each. It would be ideal to be able to design from a theoretical basis, the properties of the desired material. Since this does not seem feasible at the present, the next best approach is to try to anticipate what materials may be of value, so that experimental research time may be best utilized.

The use of empirical relations, or trends indicating general areas which are not of prime importance, can be of great help in the search for materials with good high temperature thermoelectric characteristics.

THERMOELECTRIC MATERIALS ANALYSIS

The analysis of thermoelectric materials must be based on the specific function or use for which they are considered. Just as it is true that no individual structural material is best for all applications, it is obvious that there can be no best thermoelectric material. This analysis is based on the utilization of thermoelectric materials for the conversion of nuclear power to electricity in a manner that is as efficient and economical as possible. It is known that thermoelectrics have been proposed for military and space projects, but such usage is rarely dependent on efficiency or economy.

Since the efficiency for thermoelectric conversion was shown to contain the Carnot efficiency, it is evident that direct conversion should be designed for the highest possible temperature. Conventional nuclear power reactors are likewise designed for the highest practical temperature. The usual limitation, however, is coolant technology at high temperatures, excessive pressure or corrosion. This same limitation applies to any conversion design where the conversion elements are physically separated from the reactor fuel. The obvious advantage is a conversion system that is in direct thermal contact with the heat source. The coolant would be operated at the temperature of the cold junction of the thermoelectric materials with no technology problems at

all, while the hot junctions could be operated at the highest temperature compatible with the material properties. Highest possible Carnot efficiency could thus be attained for the material chosen. Direct physical and thermal contact between the nuclear fuel cladding and thermoelectric material will require that the materials have similar mechanical properties, such as thermal expansion coefficients. In order to operate in a reactor core region, the thermoelectric materials must show good radiation effect resistance. Of course, the material must have good chemical and crystallographic stability at the proposed hot junction temperature.

It is anticipated that in the search for high efficiency materials, an adequately high proportion will have melting temperatures exceeding 1000°C , so that this may be used as a primary design parameter. Other parameters follow rather naturally from the performance specifications developed above. These are formalized in the following listing of design intentions.

General Objective:

Design of thermoelectric direct conversion system for the conversion of nuclear fission energy into electrical power.

Performance Specifications:

1. High over all efficiency
2. Low cost per unit energy converted

3. Good nuclear radiation stability
4. Good chemical and crystallographic stability
5. Reasonable mechanical properties

Design Parameters:

1. Thermoelectric materials must be capable of hot junction temperatures greater than 1000°C .
2. Thermoelectric parameters must remain stable for at least 10^{21} nvt fast neutrons.
3. Thermoelectric materials must be compatible with existing cladding materials at operating temperatures.
4. Thermoelectric materials must have mechanical properties capable of withstanding thermal stresses expected and forming techniques available.
5. Thermal expansion coefficients must be compatible with fuel material.

There are a large number of thermoelectric materials, some with desirable properties, others are worthless as direct conversion devices. In the literature, most materials studies have centered about a specific thermoelectric material and its variations.

As a result of the increasing number of known thermoelectric materials, empirical relations between desirable properties and material parameters have become evident.

The selection of a material which satisfies the

performance specifications and design parameters enumerated is directed by the use of empirical relations which have evolved with the technology. The inadequacies of the relations are apparent; however, the contradictions between such empiricism and experimental observation are indicated whenever possible.

The problem of selecting from the possible thousands of combinations of the elements, a few binary compounds or even groups of compounds which are semiconductors, is a formidable one. For this reason, relations which are of wide applicability are used first. It is generally accepted that semiconductors provide the best thermoelectric materials, since they must have reasonable electrical conductivity but low thermal conductivity, i.e. they have ideal charge carrier density values. Insulators have electrical resistivity which is prohibitively high, and metals have high thermal conductivity while their Seebeck coefficient is too small. Cornish (10) has shown a way of selecting these semiconductors from the periodic chart of the elements. The technique used is to assume that the elements will form semiconductors just as ionic compounds would be formed. Combinations of groups which would result in closed or half filled electron shells indicate areas of maximum stability and contain compounds which may be semiconductors.

Other properties to be discussed later are related to

the type of hypothetical ionic bonding proposed, hence the compounds are referred to by the following bonding types: A, T, B and B'.

Column A indicates those compounds where the electron excess of the cation exactly balances the anions electron shortage, giving a filled shell. These compounds are of an ionic nature, since the outer electrons are easily transferred. Column T represents the transition metals which could lose the necessary number of electrons and have left a stable half filled d shell. Column B contains the anion elements which would tend to share the number of electrons necessary to cause the formation of a stable electron shell configuration. The B' column are those B group elements which would lose the number of electrons held in excess of a closed shell, resulting in the formation of a second closed shell.

Compounds from the "mid portion" of the anion elements, groups IVb, Vb, and VIb (which are not completely ionic as the group VIIb halides would be) are those of greatest potential. The resulting possible compounds are shown in Table 1.

Three additional groups of compounds have been included since examples of these occur experimentally even though this analysis did not predict them.

Since the compounds contained in these groups are not all semiconductors, each group must be segregated into

Table 1. Semiconductor compounds

| Type A | Type T | Type B | Type B' |
|-----------|------------|-----------|-----------|
| IVa — IVb | VIII — IVb | IVb — IVb | VIb — IVb |
| IIIa — Vb | VIII — Vb | IIIb — Vb | Vb — Vb |
| IIa — VIb | VIIa — VIb | IIb — VIb | Others |

semiconductors and non semiconductors. Hagg (25) showed that the metallic structure of compounds is related to the ratio of nonmetallic atom to metallic atom radii. The critical ratio was found by Gambino (22) to be 0.59. When the radius ratio is less than this, the resultant structure is the normal interstitial type of metallic compounds. On the other hand, for compounds of radius ratio larger than or very near 0.59, the more complex structure may result in a semiconductor. Each of the fifteen compound groups will be considered separately and in each case, compounds which are known to be metallic or insulator will be discarded. Conversely those materials which are known to be semiconductors will be retained regardless of the radius ratio test conclusion.

The energy band gap, E_g , between the valence and conduction bands of a material is a measure of the energy required to cause a valence electron to be separated from a bond, contributing to the flow of electrical current.

Miller and Ure (51) have indicated that for materials whose E_g is less than 0.5 eV, the material is effectively metallic, since only a very small electric field is required to make the valence electrons mobile. On the other hand, for materials whose E_g is greater than 3 eV, ionic insulator characteristics are predominant. Egli (18) recommends that optimum semiconductor properties are attained for E_g between 1 and 2 eV. The criterion of E_g has proven to be of wider applicability for selecting semiconductors than the atomic radius ratio test. When E_g is known for a material, that technique will be preferentially used.

Many authors indicate trends in basic properties of semiconductors as a function of the molecular weight, M , of their compounds.

Where the E_g is not known experimentally, it may often be anticipated to order of magnitude, or better. Searcy and Meschi (66) demonstrate that E_g tends to decrease as M increases. They also note that group IV compounds have low E_g , III-V compounds have higher E_g , II-VI even higher, and the ionic alkali halides, I-VII compounds have the highest. The value of E_g apparently increases with the ionic nature of the compound.

It is observed by Heikes and Ure (27) that almost without exception, the melting temperature, T_m , decreases as M increases. This often enables one to estimate values of T_m

which are not available otherwise.

Ioffe (36) predicts a decrease in k as M increases. He suggests that heavy atoms or molecules that are weakly bound together should have the lowest k , i.e., k decreases from group IV compounds to III-V compounds to II-VI compounds. Egli (18) estimates that a good thermoelectric semiconductor should have k less than $0.01 \text{ w/cm } ^\circ\text{K}$.

Charge carrier mobility μ also appears to be a function of molecular weight. Ioffe (36) also predicts the increase of μ with increasing molecular weight, and Heikes and Ure (27) have shown this to be true for some II-VI and IV-VI compounds. Egli (18) estimates that a good thermoelectric semiconductor should have μ greater than $100 \text{ cm}^2/\text{V s}$.

By observing these trends, and noting when they are violated, it is evident that there are more violations in some types of compounds than in others. In general the A and T type compounds follow the trends quite closely. Type B compounds contain a few violators, and in type B' compounds, irregularities are not uncommon. In general, the reliability of predictions is best indicated by the uniformity of surrounding data. Hence for compound types where data are sparse, predictions are usually impossible.

Ia-Vb Compounds

These compounds show low T_m values, less than 1300°K . Available data are primarily on the metallic nitrides and antimonides. The E_g values which are known for some of the antimonides, are within the optimum region of 1 to 2 eV, and increase consistently with increasing M.

Published T_m values for these compounds are all less than 1130°K . It is expected that T_m will generally decrease as the molecular weight of a compound in the homologous series increases. The temperature T_m for the first member of this series of compounds is 1120°K , hence all others should be very close to or less than this. It is quite doubtful that any of the compounds in the series could satisfy the operating temperature requirement.

The ratio of the nonmetallic to metallic atom radii also indicates that many of the compounds are probably metallic. This applies to all the nitrides and many of the phosphides and arsenides.

None of the Ia-Vb compounds show particular promise at the present.

IIa-IVb Compounds

Magnesium and calcium compounds of the IVb group have been investigated to a certain extent. Some of them show

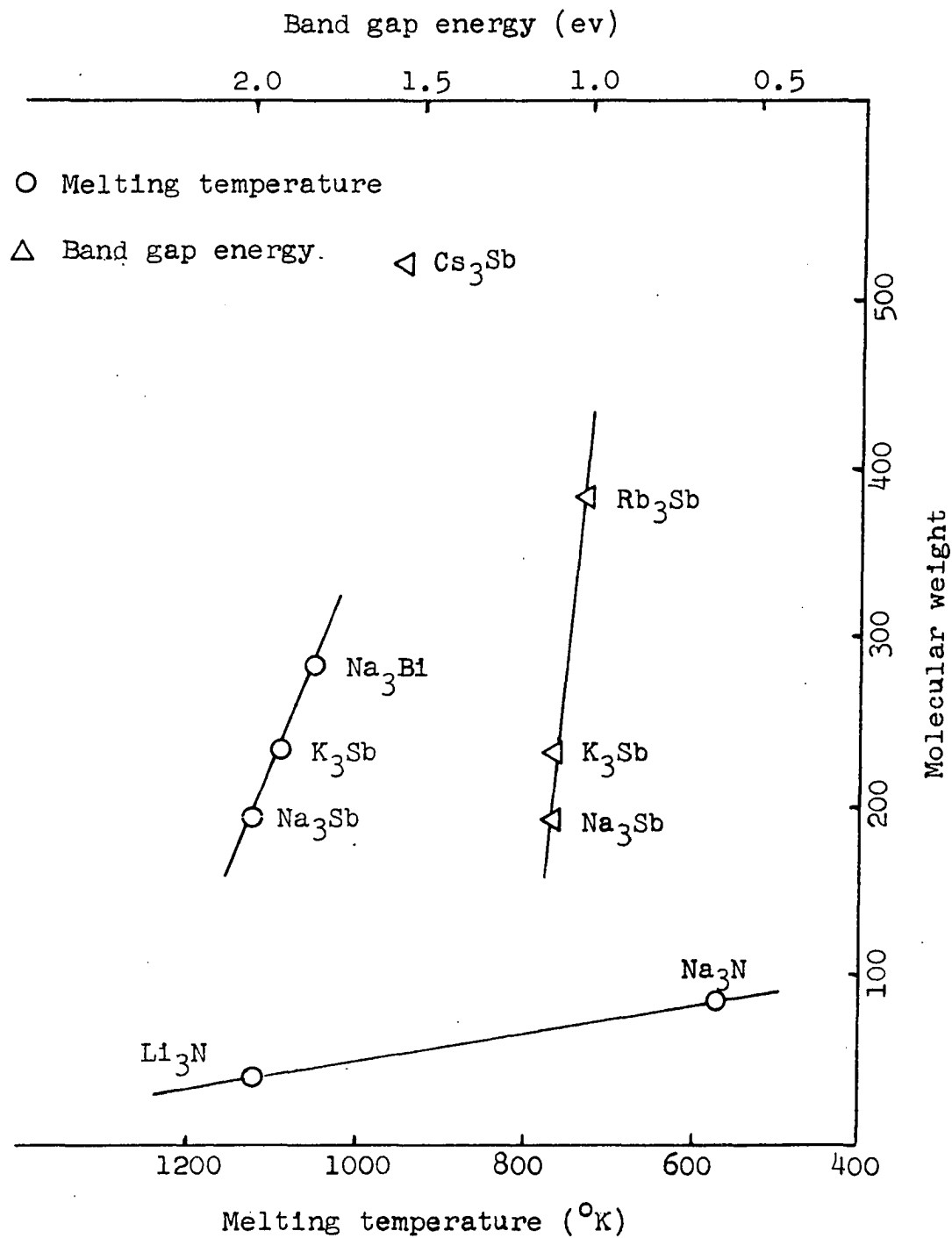


Figure 1. Ia-Vb compound parameters

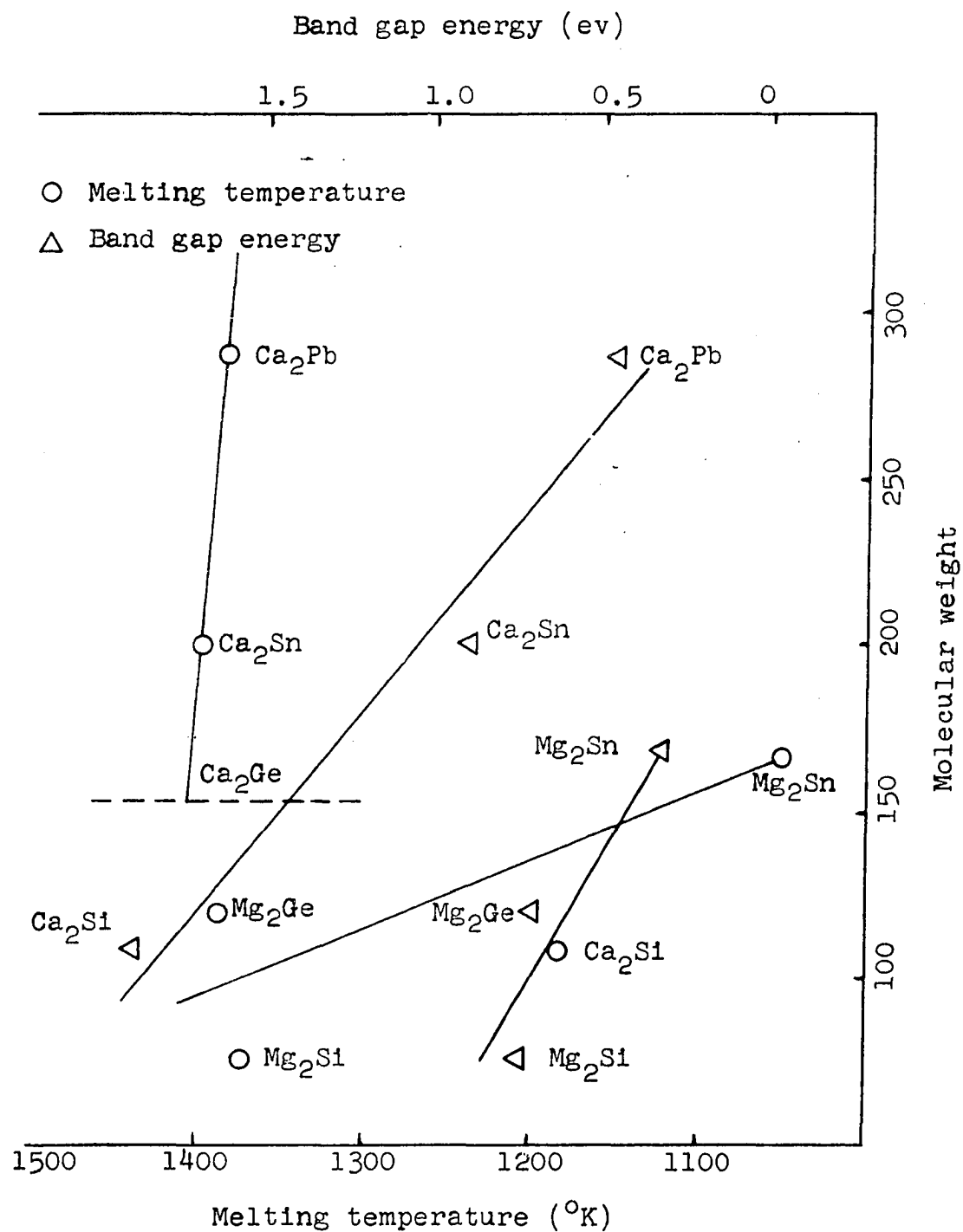


Figure 2. IIa-IVb compound parameters

high values of T_m ; however, the generally accepted rule of T_m decreasing with the molecular weight of the compound has two exceptions, both silicon compounds, in this homologous group. There are four compounds of this group which have suitable T_m values, and for two of these, magnesium germanide and magnesium silicide, most of the basic data are known, suggesting that they may be good high temperature thermoelectric materials.

Since this series of compounds has shown some irregularities, the selection of other possible materials is less reliable. Three compounds which could possibly be of interest are the germanide, stannide and plumbide of calcium. Several other parameters must be determined for each of these in order to calculate Z .

The most critical parameter for the magnesium germanide is its relatively large value of the phonon thermal conductivity k_{ph} , about $0.1 \text{ w/cm } ^\circ\text{K}$. Since a small k_{ph} , equal to or less than $0.01 \text{ w/cm } ^\circ\text{K}$, is necessary for a large figure of merit, this material is expected to be an inferior one. Unfortunately, k_{ph} is not available for magnesium silicide. The calcium compounds, however, should have a smaller value of k_{ph} since it tends to decrease as the molecular weight increases.

IIa-Vb Compounds

Compounds which have received the most attention in this series are some of the magnesium and calcium compounds. However, few data are available, and even those show some irregularities, as a result, are not graphically displayed. The fact that a compound's properties are inconsistent with the homologous series is not necessarily a detriment since some of the best thermoelectric materials have properties which do not correspond to their series. Complete basic data are available for magnesium antimonide. It has peculiarly low values of E_g and electron mobility μ , while the crucial value of k_{ph} is about $0.009 \text{ w/cm } ^\circ\text{K}$, hence a very good prospect. Calcium phosphide, has suitable T_m and E_g , classifying it as a possible thermoelectric material. Calcium phosphide shows semiconductor characteristics by its atomic radius ratio and the relatively large value of E_g , 2.2 eV.

High temperature nitrides of all the IIa compounds also occur in this series; however, the ratio of nonmetallic to metallic atom radii indicates that they are probably metallic.

IIb-Vb Compounds

Most interest in this homologous series centers around the arsenides and antimonides of zinc and cadmium. Cadmium antimonide has an acceptable value of k_{ph} , about $.01 \text{ w/cm } ^\circ\text{K}$,

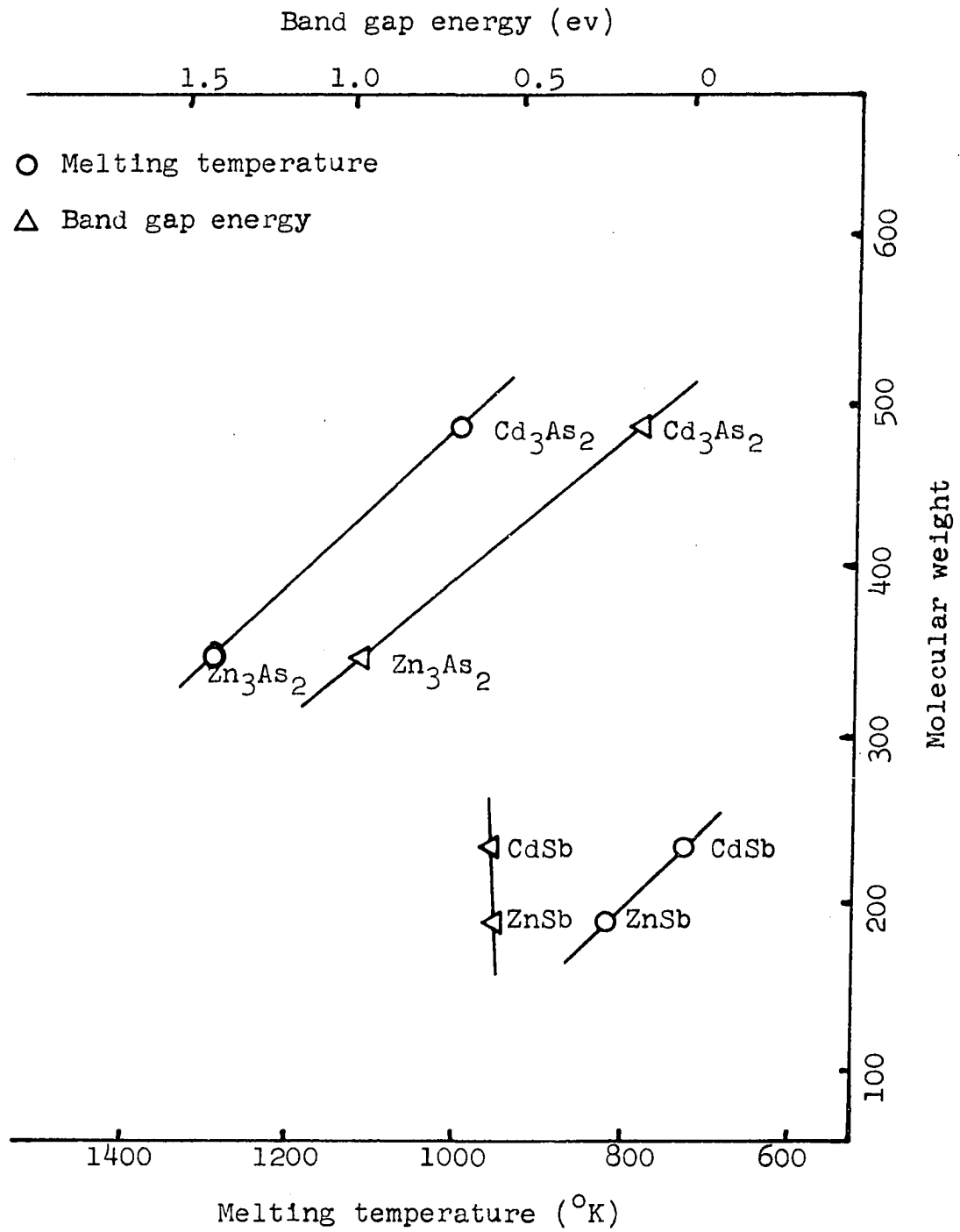


Figure 3. IIb-Vb compound parameters

but its T_m is too low. Lower molecular weight implies higher T_m and this is true for the arsenide; however, the T_m is still not high enough. The difference in crystal structure is possibly the cause of a ten-fold increase in k_{ph} making it useless. None of the other known materials of this series appear promising.

A possible material is cadmium phosphide, providing its T_m is above 1300°K and the other basic parameters do not differ much from the arsenide.

IIa-VIb Compounds

Data should follow quite regular patterns in this group since it is type A, the most reliable for predicting unknown properties of compounds in the series.

This series shows an excellent range of T_m values; however, the energy band gaps, E_g , that are available indicate that the series probably consists of ionic insulators. Since E_g decreases with increasing molecular weight, it is expected that all the compounds lighter than barium sulfide will be insulators as well. The only possibilities for semiconductors in this series are barium telluride and selenide, since their T_m should be less than 2200° , and E_g should be less than 3.6 eV. It is predicted that BaSe will have E_g between 1 and 2 eV and T_m between 1500° and 2000°K , quite ideal.

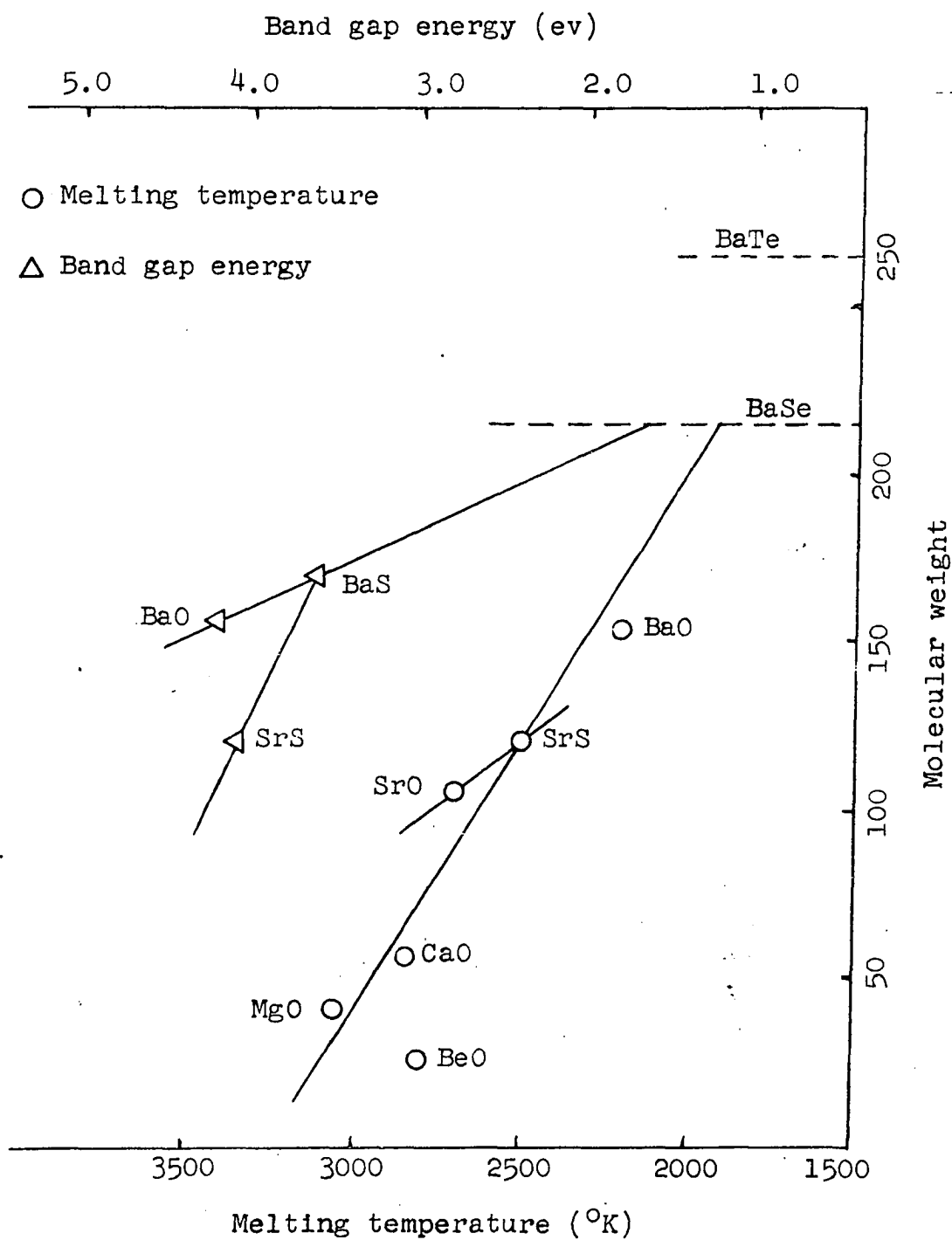


Figure 4. IIa-VIb compound parameters

IIb-VIb Compounds

This series is a member of the B type, where a few irregularities should be expected. Only the oxide and sulfide of mercury do not follow the trends and appear to be the major if not only irregularities.

Two members of this homologous series show excellent values of k_{ph} , less than $0.01 \text{ w/cm } ^\circ\text{K}$. One of these, zinc oxide, has too large an energy gap unfortunately, indicating that it is an insulator. The remaining compound for which acceptable basic data are known is cadmium oxide. Cadmium sulfide, selenide, and telluride also show good values of T_m and E_g and if they follow the expected trends, their values of k_{ph} should be just as low or lower.

Similarly, zinc selenide and telluride have suitable T_m and E_g values. It is possible that they may also follow the expected trend in values of k_{ph} resulting in very low values. Zinc oxide and sulfide show values of E_g which label them as insulators whose other basic parameters would otherwise make them very interesting.

A total of five possible thermoelectric compounds and one probably thermoelectric compound are found in this series.

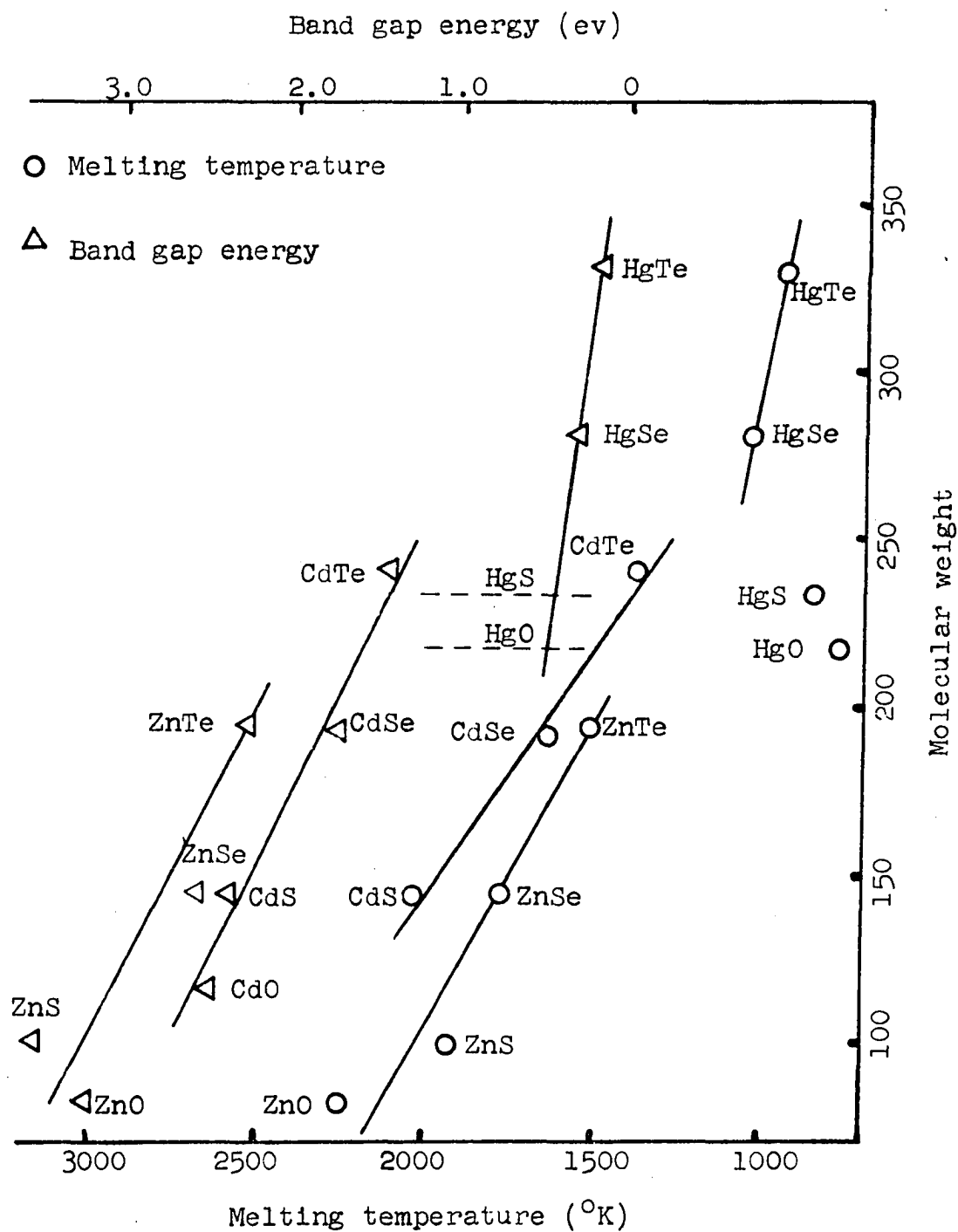


Figure 5. IIb-VIb compound parameters

IIIa-Vb Compounds

This homologous series was predicted by the pseudoionic bonding technique as a possible series of semiconductors of the reliable type A. None of these compounds has been widely investigated, or at least basic parameters have not been published, and are not graphed.

The only additional information known about these materials is that their nitrides are all metallic. Possibly the remainder of the compounds are also metallic or semimetallic.

IIIb-Vb Compounds

This homologous series demonstrates most of the parameter trends quite clearly, with no flagrant violations, in spite of the fact that it is type B. T_m , E_g and k_{ph} all decrease, and μ increases continuously with increasing molecular weight.

It can be seen that most of the high temperature boron compounds are insulators. Similarly aluminum nitride and phosphide also have values of E_g too large to be semiconductors. The arsenide and antimonide of aluminum both show good properties, except for the fact that their k_{ph} must be larger than 0.37 and 0.27, which are already too large. It is possible that aluminum bismuthide may have a suitable combination of basic data, but the predicted values do not

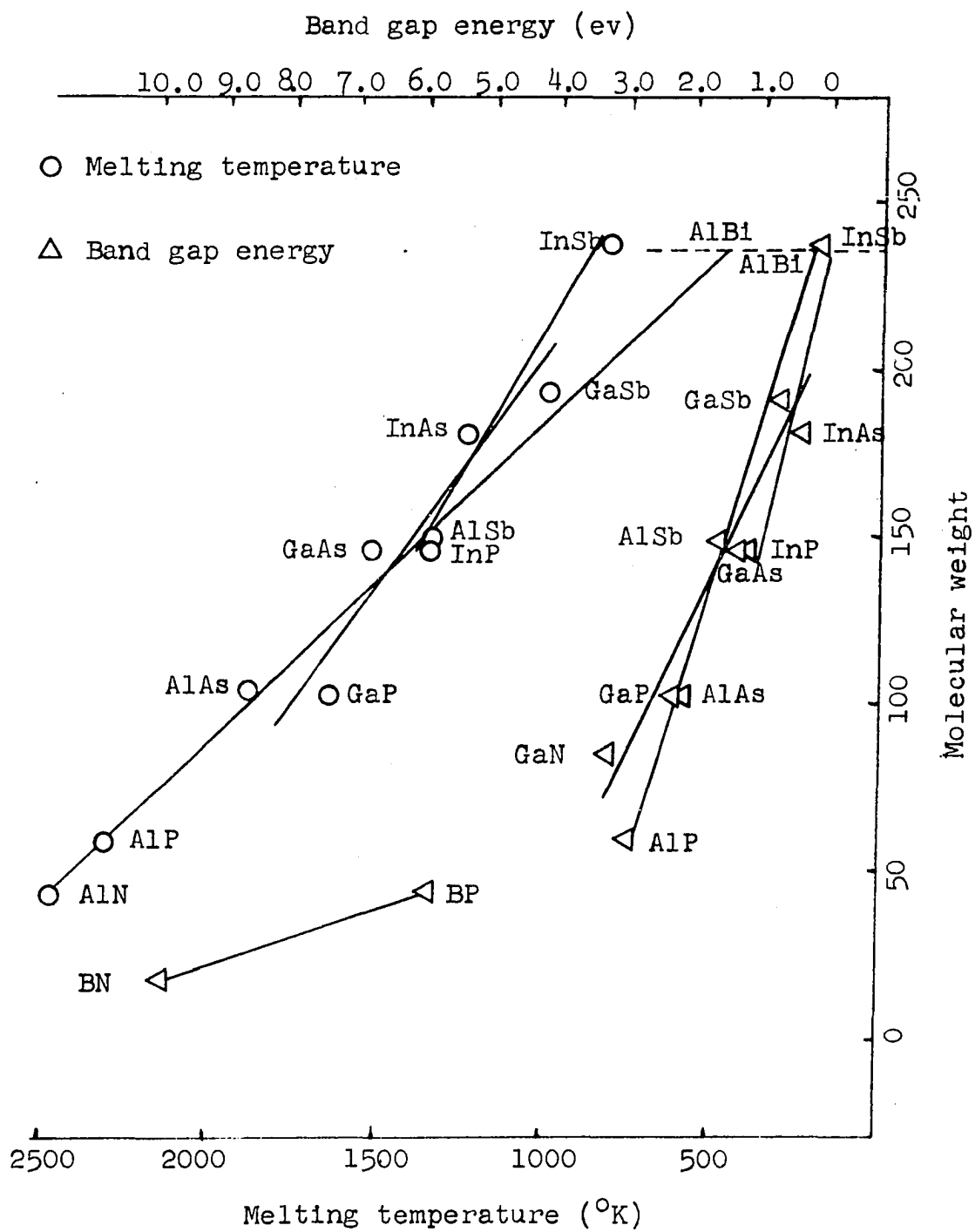


Figure 6. IIIb-Vb compound parameters

look promising.

The remainder of the compounds either have too large a value of k_{ph} , or too low a T_m temperature. Even though these data are not available experimentally, it can be seen from the trends that k_{ph} will be larger than 0.1, and many of the T_m will be less than 1300°K.

IIIb-VIb Compounds

The IIIb-VIb series of compounds is actually a double set, e.g. gallium telluride and gallium sesquitelluride. The sesqui compounds have received the most attention. All of the boron compounds and most of the aluminum compounds have large E_g values indicating that they are insulators. The remaining aluminum compounds are not high temperature ones. Of the gallium compounds, only the sesquiselenide shows good properties, in particular, an excellent k_{ph} of about 0.005 w/cm °K is observed. The other compounds of gallium have either low T_m or an E_g that is larger than 2 or 3 ev.

Indium sesquisulfide may be a possible thermoelectric material. It has reasonable values of T_m and E_g , but k_{ph} is unknown.

IV-IVb Compounds

There are not enough data available on most of these compounds to indicate promising thermoelectric materials.

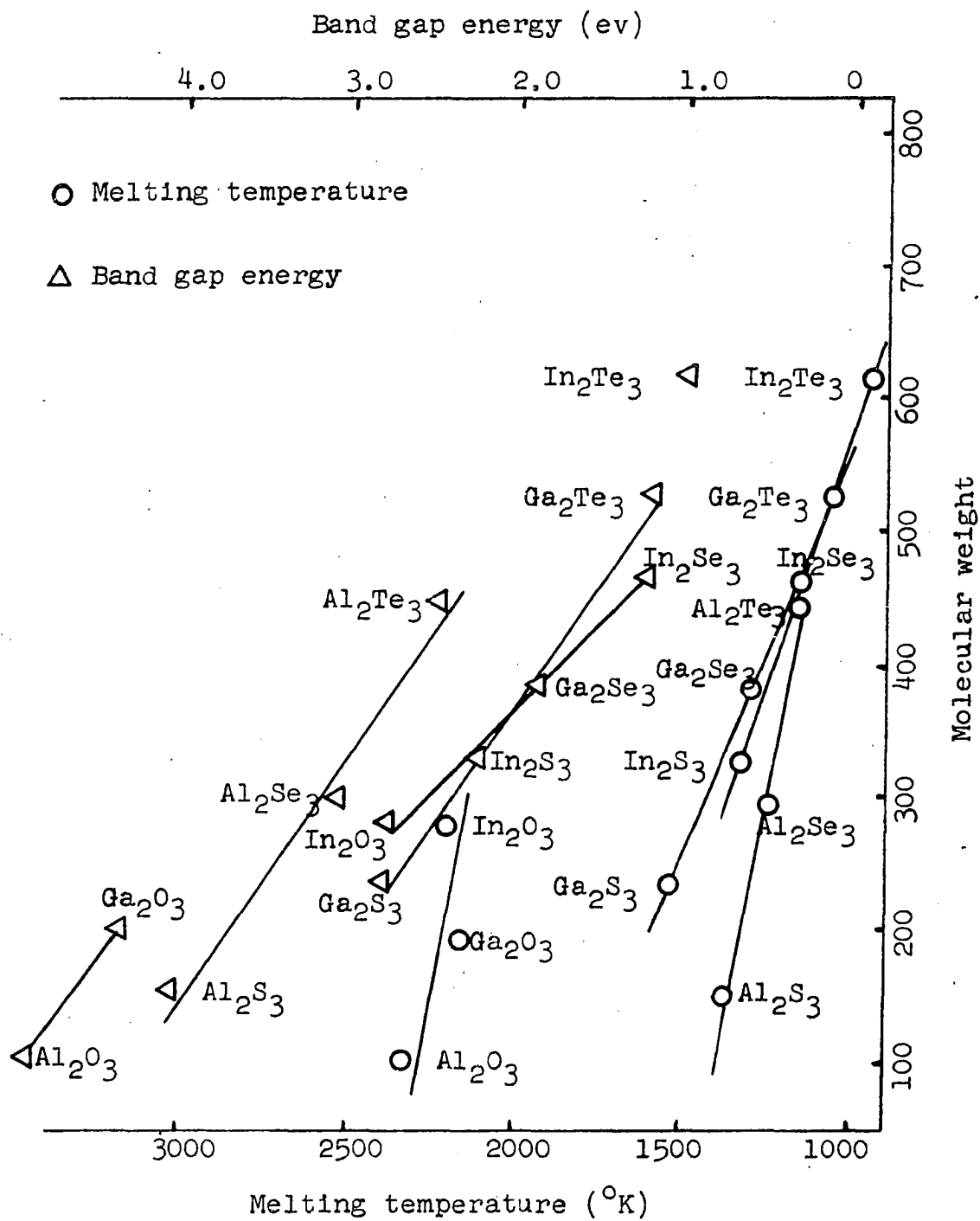


Figure 7. IIIb-VIb compound parameters

Experimental data on germanium silicide show good values for ρ , S and k , indicating great promise. No information is given for E_g or μ so it is difficult to speculate on surrounding materials, and data are not graphed. There are two silicide compounds which might show promise however. They are titanium silicide and zirconium silicide. Other known compounds have values of k_{ph} which are too high, greater than $0.1 \text{ w/cm } ^\circ\text{K}$.

Nothing appears to be promising in the IVa-VIb compounds. These compounds have not been discarded for any reason; it is just that not enough is known about them to suggest possible thermoelectric use.

IVb-VIb Compounds

Major interest in this series of compounds centers in the compounds of tin, lead, and to a more limited extent in those of germanium. Unfortunately, germanium and tin compounds have low T_m values. Silicon compounds may be of interest, but too little is known of them.

There are two potential thermoelectric materials in the lead compounds, lead sulfide and lead selenide. The T_m of the oxide and telluride are less than 1300°K and too low to be of use.

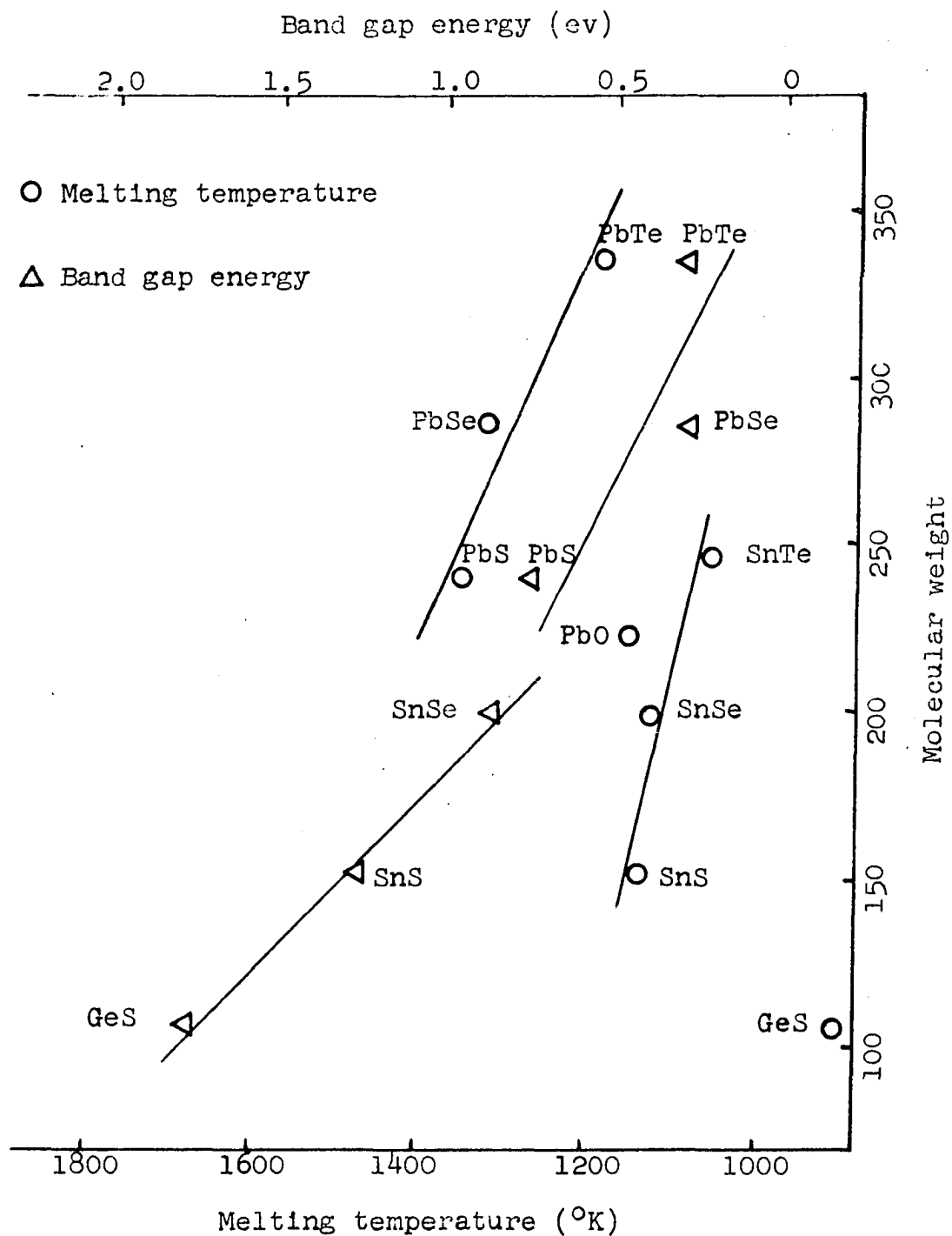


Figure 8. IVb-VIb compound parameters

V-V Compounds

Few basic data are known for these compounds; however, high values of T_m for some of the nitrides are observed. On the other hand, it is seen that the nonmetallic to metallic atom radius ratio indicates that all of these nitrides should be metallic. Published values for the resistivity of niobium and tantalum nitrides, 200 and $135 \mu\Omega$ respectively, indicates that they are semiconductors, hence are possible thermoelectric materials.

Vb-VIb Compounds

There are several compounds in this series which exhibit very good thermoelectric properties; however, they are all low temperature materials, T_m less than 1300°K . Thus none of them are of possible interest for the present design.

VIII-Vb Compounds

This series of homologous compounds contains the transition metal nitrides. These nitrides are less ionic than the oxides (17) and as a result, the valence electrons of the metal atom are not all held in localized bonds. Hence a metallic nature predominates. Phosphorus, arsenic and antimony atoms have even less attraction for the metal atom valence electrons, and are even more metallic.

If values of E_g were known for these compounds, it would be obvious that none had the properties of semiconductors. Small values of E_g would be evident for the nitrides, less than .1 ev, and they would get smaller for the heavier compounds.

VIII-VI Compounds

Information is rather sparse on these compounds; however, due to the high T_m and acceptable E_g for iron sesquioxide and iron sulfide, they are possibilities. The sesquisulfide and sesquiselenide compounds should have lower values of both T_m and E_g , and unless they fall too low these compounds may also be possible thermoelectric materials.

Nickel oxide has a very high T_m , reasonable E_g and good k , ρ and S data; it shows great promise and is calculated for comparison.

Cobalt oxide and sulfide are the only other compounds which show T_m values greater than 1300°K . Since they may have good values of E_g , they may also be acceptable.

IIIa-VIb Compounds

Very little information is available for these rare earth oxides and sulfides. Cerium sulfide compounds have received the most attention; however, all are expected to be high temperature materials.

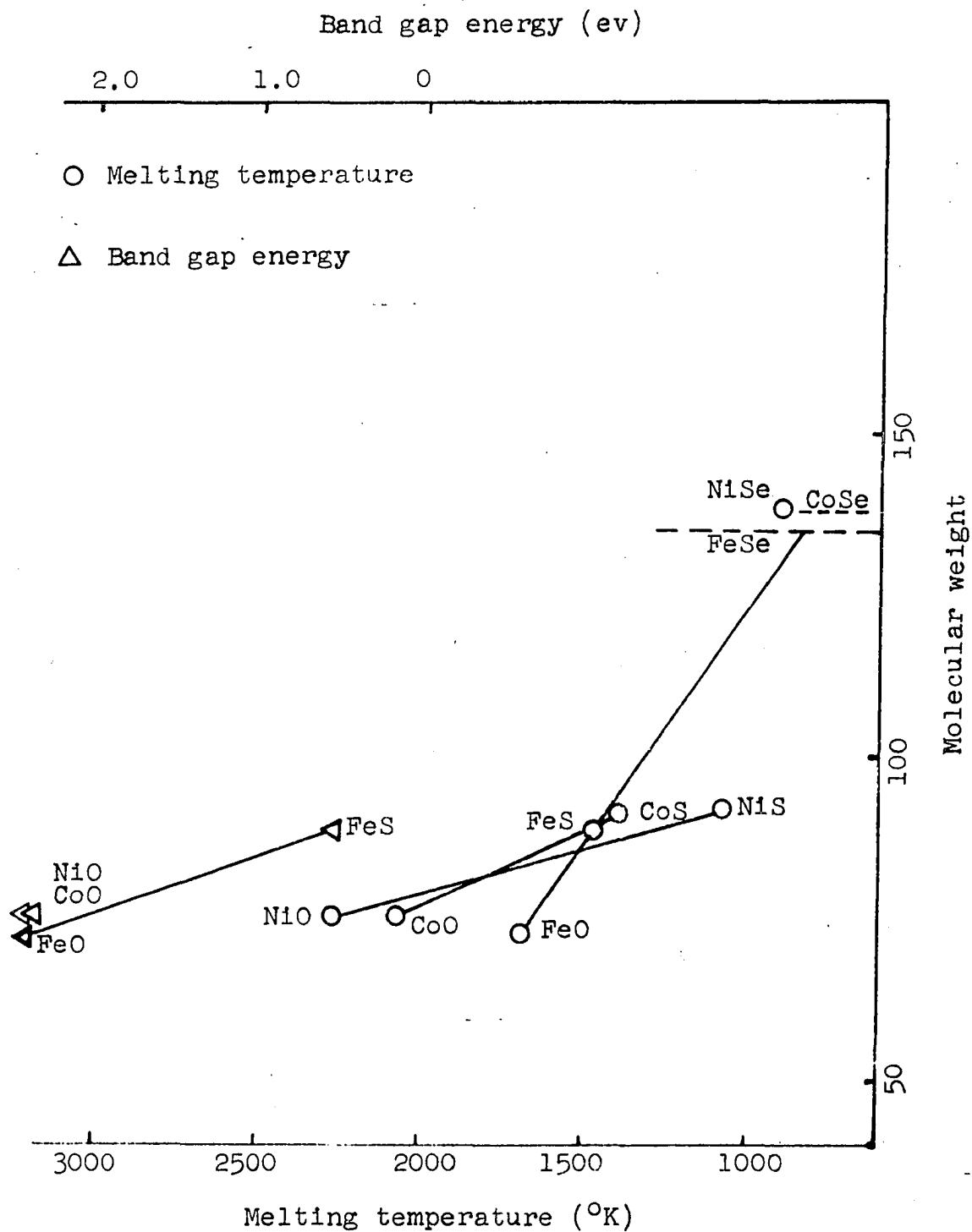


Figure 9. VIII-VI compound parameters

Basic information is known for cerium oxide and sulfide and for chromium silicide, allowing these to be calculated. It is also predicted by Kurnick et al.(45) that all will have low k_{ph} . Apparently then all others satisfy the minimum requirements of a possible thermoelectric material.

The group by group survey of binary compounds in quest of semiconductors which are or might be thermoelectric materials has resulted in seven probable and twenty nine possible thermoelectric compounds.

A simple segregation of elements according to their neutron absorption cross section is utilized to separate out unsuitable materials. Since the thermoelectric material is specified to operate for an integrated thermal flux time of 10^{21} nvt, a material of activation cross section, $10b$, would undergo approximately 1% transmutation; this value is chosen as the practical limit.

The number of compounds whose constituents have cross sections less than $10b$ is six of the probable and eighteen of the possible thermoelectric materials. These are shown in Tables 2 and 3 which include pertinent bibliographic references.

The figure of merit is calculated for each material where sufficient data are available. Most materials are investigated as single crystals as well as polycrystalline ingots. As pointed out by Ioffe, the dopant may play a

Table 2. Possible thermoelectric materials

| Compound | Bibliographic reference |
|----------|-------------------------|
| AlBi | |
| BaTe | |
| CaGe | |
| CaP | (66) |
| CaPb | {44} |
| CaSn | {44} |
| CrS | {39} |
| FeO | {47,53,54,69,80} |
| FeS | {16,21,29,31,61,71} |
| LaO | {11,24,34,59,76} |
| LaS | {11,45,76} |
| MgGe | {28,62,78} |
| MgSi | {28,62,73,78,80,81} |
| NbN | {55} |
| PbS | {8,20,61,64,70,80} |
| TiSi | {49,56,63} |
| ZnTe | |
| ZrSi | (49,56,63) |

Table 3. Thermoelectric materials of calculable figure of merit

| Compound | Bibliographic reference |
|----------|--------------------------------------|
| CeO | (3,6,11,12,32,40,55,49,60,76) |
| CeS | {2,6,7,9,12,14,15,16,38,50,51,76,77} |
| CrSi | {16,23,43,46,56,57,58,63,73,74,77} |
| GeSi | {1,4,30,58,68,72,73,81} |
| MgSb | {16,48} |
| NiO | (12,14,21,34,52,54,55,65,75,76) |

significant role in the determination of the k_{ph} and Z , hence materials are considered with different dopant. Complete data was found for fourteen such materials or modifications; seven of these showed superior characteristics. All of the seven were polycrystalline solids.

Polycrystalline solids are usually preferred for thermoelectric conversion, due to their isotropic properties, ease and cost of preparation, and usually lower k_{ph} . Many semiconductor materials are somewhat brittle; however, one of these, magnesium antimonide, is quite malleable.

Thermoelectric direct conversion is most efficient for a couple formed by a p type and an n type material. Calculations are made for each possible combination of the seven materials based on optimum temperature conditions for each combination.

Harman (26) has shown that maximum theoretical efficiency may be expected for a thermoelectric couple if the hot junction is operated at about $0.9 T_m$. This is very near the highest practical temperature as far as the mechanical properties of the material are concerned, but still represents a relatively high Carnot efficiency. In addition, the k_{ph} usually decreases with increasing temperature, giving a high temperature increase to the figure of merit. It has also been shown that the cold junction temperature should be about $1/3$ to $1/4$ the hot junction temperature; however, this is not

critical.

The figure of merit Z_{12} , and couple efficiency η_{12} are calculated, for each pair of materials 1 and 2.

$$Z_{12} = \frac{(S_1 - S_2)^2}{\left[(k_1 \rho_1)^{\frac{1}{2}} + (k_2 \rho_2)^{\frac{1}{2}} \right]^2}$$

$$\eta_{12} = \left(\frac{\Delta T}{T_h} \right) \frac{\left[(1 + \bar{T} Z_{12})^{\frac{1}{2}} - 1 \right]}{\left[(1 + \bar{T} Z_{12})^{\frac{1}{2}} + T_c/T_h \right]}$$

Two superior combinations are evident, chromium silicide, germanium silicide with an overall efficiency of 14.8% and magnesium antimonide, germanium silicide, with an efficiency of 15.3%. Both operate at a hot junction temperature of 1345°K or 1072°C . Their efficiencies are so close that the ultimate decision for an actual device would have to be based on an experimental evaluation of the compatibility of the conversion couple with the system, a rather complete engineering analysis.

However, lacking such necessary experimental information, and even basic information such as thermal expansion coefficients, the couple with the highest over-all efficiency is used as the basis of a design analysis for a nuclear reactor core, and the conversion of its generated heat into electricity.

One consideration which does not fall within the realm of the usual engineering analysis of the compatibility of a sub system to the prime system, is the problem of radiation damage. This is a particularly difficult area, and is not at all well understood. Models which agree with experiment for some materials or situations, do not apply to others, pointing out that although radiation effects models may be successful in some instances, they are not complete, and analytical predictions based entirely on a model are probably unjustifiable.

Thermoelectric materials are subjected to essentially only gamma rays and neutrons in a nuclear reactor, charged particles need not be considered. The interaction of gamma rays with the thermoelectric material is primarily an ionization process. However, since thermoelectric materials have low electrical resistivity, the ion pairs formed recombine readily, leaving little or no anticipated residue. Fission neutrons interact with the materials as a function of their scattering cross section. A high energy interaction probably results in ionization with the same net result as a gamma ray induced ion pair.

The effect of ionization is often referred to as a transient radiation effect, since ionization is formed in the semiconductor and continues to exert an influence on the material properties until the ion pairs recombine. Recombination

of the electron and vacancy or hole takes place at defects in the crystalline lattice which are called recombination centers (67). These recombination centers are associated with the energy levels of the forbidden energy band gap, i.e., the number of donor or vacancy levels present in the band gap. Ultra pure semiconductors such as are commonly used in electronics, have very few recombination centers, and resultant long lifetimes for the electrons and holes formed by ionization. Life times of 1 μ second to 1 m second mean a high concentration of excess or ionization charge carriers, and a drastic change in the semiconductor's electrical properties. Thermoelectric materials on the other hand usually have an impurity concentration of about $10^{19}/\text{cm}^3$; hence, a high density of recombination centers and very short electron and hole lifetimes before recombination. As a result, there is an insignificant transient effect to the electronic properties of such thermoelectric materials.

At energies below the threshold for ionization production, dislocation pairs are formed. This Frenkel defect as it is sometimes called is composed of a vacancy in the lattice and an interstitial atom. Both of these defects are more or less free to move, but generally have different diffusion coefficients, etc. Movement of the interstitial or knock-on, as it may be called when it is in motion, may result in the formation of additional displacements or

secondary knock-ons, and a sharing of the primary knock-on's energy. Thus, a high energy primary knock-on may result in the formation of an area with a high density of dislocations or defects called a thermal or dislocation spike. Such an area of disorder and distortion in a semiconductor crystal can dramatically affect all of the basic properties upon which the thermoelectric effect depends, usually resulting in a degradation of the figure of merit for the couple.

The concept of the annealing of these defects is not well understood either. It is known that the different defects anneal at temperatures which are a function of their mobility or diffusion properties. Experimentally, it is observed that there is a critical temperature range above which material properties return to their preirradiation values. It is assumed that above this temperature, the rate of defect formation is exceeded by the rate of anneal for that defect. It is proposed by Howe and Siegel (33) that even though high temperature use may assure the annealing of dislocations or Frenkel defects, a dislocation spike may still result in a crystal jog or stacking fault.

It is not certain how this would become apparent in thermoelectric materials, but it would be expected to be more pronounced in single crystals than it would be in polycrystalline ingots or powder metallurgically formed slugs. Probably the two latter forms would be preferable, all other

parameters equal.

The parameter which is usually most affected in the irradiation of semiconductors is the electrical resistivity (42). This is an easily measured parameter, and has become the most common method of observing radiation damage. The over-all resistivity of a thermoelectric couple usually increases with radiation. The four probe measurement technique (26) shows that the resistivity of the thermoelectric material decreases, but the resistivity of the electrical junction bonds increases markedly with accumulated radiation dose. The Seebeck coefficient increases somewhat, but the combination S^2/ρ decreases, indicating the relative importance of the electrical bond. The lattice or phonon component of the thermal conductivity, k_{ph} , also decreases as a result of radiation induced defects, primarily by lattice disordering, and the creation of trapping centers. The net effect to most thermoelectrics is a decrease in the figure of merit and over-all efficiency.

It is generally agreed (33,27) that thermoelectric operation should be satisfactory if it is operated above the annealing temperature. For PbTe the annealing temperature is about 150°C, for Bi₂Te₃ and GeTe about 200°C. Most materials show complete annealing at 200-300°C, hence operation of thermoelectrics should be designed for temperatures in excess of this.

Very little experimental information is available, however, for thermoelectrics which have actually been operated at temperatures above the annealing temperature. A good deal of experience has been obtained with the SNAP program and the use of PbTe. Two systems which have been tested for reactor operation and published (13,41,42) have shown a marked degradation in power output as a function of flux time. This result was not anticipated, and even an increase in operating temperature though temporarily beneficial, did not permanently reverse or inhibit the deterioration trend. No explanation has been given; perhaps the electrical bonding problems have not been solved. It is obvious that the radiation effects on thermoelectrics are not completely understood, for there appears to be a wide discrepancy between the expected and actual behavior of these materials.

Although it was not expressly stated, it was assumed that the entire thermoelectric element was operated above the critical temperature. If this were not true, this might be the answer to the failure. Certainly a temperature gradient across the thermoelectric which included the critical temperature would suggest that radiation damage could accumulate in the cold end. The accumulation would be primarily due to formation of radiation defects which could not anneal out. It has also been suggested that the temperature gradient may cause the migration of lattice dislocations to areas of lower

temperature within a crystal; this effect may also contribute to the accumulation of radiation damage at low temperature. Another problem which apparently has not been considered is the formation of crystal jogs or stacking faults caused by dislocation spikes at temperatures exceeding the annealing temperature. Perhaps either of these may be partially responsible for the deterioration of the cell power output.

There is little theoretical ground for choosing one thermoelectric material in preference to another as far as radiation damage is concerned. Based on the fact that the energy transferred to a thermoelectric atom from a fast neutron due to a scattering collision is inversely proportional to the atomic weight, less energy transferred would mean fewer displacement spikes, hence magnesium antimonide with a larger A may be preferred.

In the absence of any additional evidence for the support of one material over another, such as is the case here, an experimental evaluation should be made of the two materials. Morphology should also be considered since crystal defects and their diffusion or stability may play an important part in the radiation effects above the annealing temperature.

Magnesium antimonide appears to have a slight advantage for use as a reactor core thermoelectric direct conversion

material. A system design will be based on the assumption that it would be found acceptable after an experimental evaluation.

NUCLEAR THERMOELECTRIC DIRECT CONVERSION SYSTEMS

System Design I

The first design consideration is based on the concept of thermoelectric direct conversion as the sole means of electric power production. The incentive for this design being a compact high power density source that is dependable and maintenance free for its useful lifetime, rugged enough to be used as a transportable unit, possibly for space application.

Since heat that is rejected at the cold junction is lost to the system, highest possible Carnot efficiency is achieved by using the lowest possible cold junction temperature. The ultimate limitation here is the necessity of using thermoelectric materials at temperatures exceeding their critical annealing temperatures. Lead telluride has the lowest temperature of the well known low temperature materials, hence the coolant temperature can only be chosen after a material can be proven to be reliable in conversion operation in a reactor at that temperature. The low temperature thermoelectric materials are comparatively well known, hence pending their suitability in a radiation environment at that temperature, one may be selected. That aspect of the problem will not be considered further here.

The problem of the staging or bonding of one

thermoelectric to another is not insignificant either, but it has been solved by isostatic pressing and sintering of the materials in a powder form.* Diffusion barriers as well as "thermal shoes" may be formed by this technique.

The use of staging or cascading is decreed by the desire to operate over the largest possible temperature drop to maintain high Carnot efficiency, yet operate the thermoelectric material at a temperature above the critical annealing temperature. In a cascade design, two or more thermoelectric couples are arranged so that the cold junction of one is thermally connected to the hot junction of the next. A staging design is based on the use of more than one material in each of the couple's legs. Thus a staged couple may consist of four or more individual materials thermally and electrically bonded in series.

The efficiency of either of these compound systems is superior to that of a simple thermoelectric couple. The primary reason for this is that the figure of merit for any material is a function of temperature, hence low temperature materials may be used where their efficiency exceeds the best high temperature materials.

*Gates, J. E. Battelle Memorial Institute. Columbus, Ohio. Thermoelectric bonding techniques. Private Communication. 1964.

In order to evaluate best the proposed high temperature direct conversion system, a cool stage using lead telluride (or any other suitable low temperature thermoelectric material) will be incorporated into the design. Based on this, the system coolant will be assumed to be water at 170°C . There is a wealth of technology available and essentially no problems involved with low temperature, low pressure water. In addition, it provides significant reactivity worth to a reactor core which contains a large quantity of thermoelectric material, potential neutron poison.

The physical dimensions of the direct conversion fuel cell are fundamentally based on the thermal conductivity of the components. Once a thermoelectric material has been chosen, the power output of the cell is a function of the volume of thermoelectric material present. The cell voltage is a function of the thermoelectric properties, but volume determines the cell internal resistance, hence current output. Increasing the volume of thermoelectric results in a decrease in the cell resistance, for a constant area. If the power production is related to the optimal use of the nuclear fuel which provides the heat source, then it is apparent that a large ratio of thermoelectric material volume to nuclear fuel volume is desirable. This is equivalent to the consideration of power density in conventional reactor core analysis.

Calculations based on the expected temperature drop across the thermoelectric material, 1070°C to 170°C , and the centerline temperature of a fuel such as UO_2 , 2760°C , indicate preferable cell geometry. A heat transfer calculation (Appendix A) for a fuel element slab, bounded on two sides by thermoelectric material which is in turn bounded by coolant water at 170°C , shows a volume of thermoelectric to volume of fuel ratio of 0.144. A similar calculation (Appendix B) for a cylindrical fuel element surrounded by a concentric cylinder of thermoelectric material has a thermoelectric to fuel ratio of 0.331. Probably spherical geometry would prove to be even better; however, spherical conversion cells do not appear to be as adaptable to reactor core incorporation as the cylinder or slab geometry. This design will thus be based on cylindrical geometry.

Selection of preferable fuel material must be a function of several criteria. Of basic consideration is the power density, which for "conventional" thermal reactors falls in the range from 2000 to 4000 Kw/Kg U^{235} . The fuel material must be able to sustain the thermoelectric hot junction at a temperature of 1070°C while remaining dimensionally stable. This requirement precludes the consideration of metallic uranium. The fuel material and coolant must be compatible to safeguard against the failure of cladding.

There are at least three fuel materials which would

satisfy the general requirements, uranium carbide, oxide, and dispersions of either. Uranium carbide is considered first; it has very good thermal conductivity and a high melting point. A heat transfer calculation similar to that in Appendix B but based on UC shows a much lower ratio of thermoelectric volume to fuel volume than is shown for UO_2 . The fundamental difference between the two is the thermal conductivity, indicating the desirability of matching the thermal properties of the fuel and thermoelectric in order to establish the proper thermal gradients. The actual power density corresponding to the use of UO_2 is approximately an order of magnitude too low by usual reactor standards, being only 226.5 Kw/Kgm U^{235} . This could be raised by using a material of nearly the same thermal conductivity but greater dilution of U. A ceramic dispersion of UO_2 satisfies this requirement as well as the high temperature and coolant compatibility qualifications. Parameters are available for beryllium oxide containing uranium dioxide in concentrations of 10, 47, and 70.9%. These dispersion concentrations are used for heat transfer calculations, the 10% UO_2 dispersion shows a much superior power density, equivalent to high enrichment thermal reactors. Unfortunately a rather large volume of fuel, i.e., 4.90 cm radius fuel rod, is necessary to maintain the desired temperature distribution across the thermoelectric materials. A 47% UO_2 dispersion requires a

fuel rod radius of 3.32 cm, a radius of 2.18 cm is specified for a 70% UO_2 dispersion, and 100% UO_2 may be used in a fuel rod of only 1.48 cm radius. Power densities vary from 54.2 w/cm^3 to 14.7 w/cm^2 or 623 Kw/Kgm U^{235} to 4,900 Kw/Kgm U^{235} , based on 1% enrichment, for 100% UO_2 and 10% UO_2 respectively.

All of these systems offer equivalent thermoelectric over-all efficiency. Different fuel concentrations may be used to optimize some other critical design criterion. A common one would be the cost per Kw of power output. Specific items which would be important in the over-all cost of the reactor as a function of its size, include the cost of the thermoelectric materials.

The reactor conversion system might also be optimized for weight or volume, possibly of prime importance in the consideration of a space or mobile power source. These or any other optimization could be easily performed with the use of a computer code, such as AIM-6. This would be the next step in determining the actual design parameters, based on the consideration of the general objectives of the design.

In order to show that a reactor conversion system based on one of these fuel combinations is feasible from a reactor physics point of view, detailed calculations are performed. These calculations, Appendix D, are based on a rather arbitrary choice of fuel, 47% UO_2 , 53% BeO . This material is

selected because it has a good power density, reasonable dimensions, but primarily because a large percentage of absorber must be present in the core; thus a cell criticality calculation for this materials configuration is a good test of criticality for the cell design in general.

Beginning with the geometry and dimensions of fuel and thermoelectric which have been previously determined by heat transfer calculations, the volume of moderator coolant is calculated. Since water at about 170°C must serve both functions, it must satisfy both requirements of highest possible reactivity and adequate volume to remove the heat.

A heterogeneous optimization process is performed to calculate the optimum ratio of fuel to moderator atoms which result in the maximum value of cell reactivity. It is assumed that the fuel is a homogeneous mass of UO_2 , BeO , and thermoelectric material (a conservative assumption). The quantities of all these are known. Equivalent macroscopic absorption cross sections, diffusion coefficients, densities and atomic weights are calculated, then used in the optimization of the ratio of fuel atoms to moderator atoms. This conclusion is then converted to a coolant flow channel for the fuel conversion cell, and a heat transfer, flow rate calculation is performed which shows the volume of coolant is adequate to remove the heat generated.

A series of criticality calculations is next performed,

based on changes in the uranium enrichment. The desired enrichment is as low as possible for economic reasons, but high enough to yield a cell multiplication factor greater than one.

These calculations are outlined in Appendix D, and show that for a BeO dispersion of 53%, a reactor core of the proposed cell geometry becomes critical at an enrichment of 3 to 4%. Precise calculations of this nature would be performed by the AIM-6 computer code, taking all of the design parameters into consideration.

The overall efficiency of the thermoelectric direct conversion system is based on an efficiency calculation for segmented thermoelectrics (27), Appendix E. This efficiency of about 31% is several times higher than current thermoelectric devices, but is significantly lower than that of central station steam turbogenerator power. The actual efficiency which must take into consideration contact resistance, and possible power inversion or transformation is probably 28 or 29%.

Based on the reactor conversion system for which calculations are made, the power generating capabilities are about 6.3 w/cm^3 of fuel. This is equivalent to 218 w/cm of fuel cell.

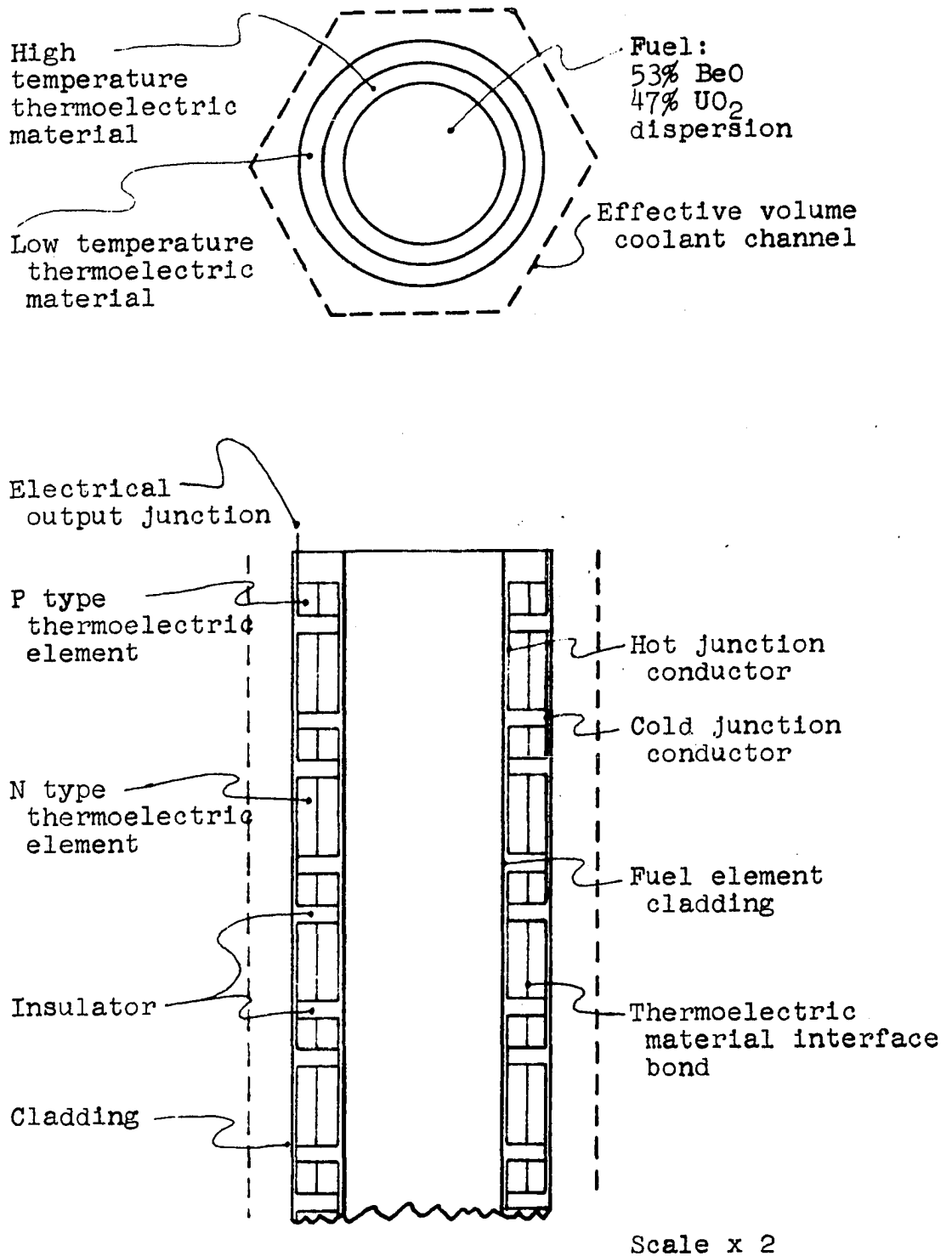


Figure 10. Nuclear direct conversion fuel element

System Design II

Although efficiencies available in design I are good, they are not equivalent to stationary plant efficiencies. However, this does not necessarily rule out thermoelectric conversion for commercial power.

The fact that high temperature thermoelectrics must be operated above some annealing temperature, relying on some other facility for utilization of lower temperature thermal energy, suggests the possibility of using thermoelectrics as a topping device for steam turbogenerating facilities. The use of high temperature thermoelectrics increases the Carnot efficiency significantly, but the fact that coolant remains at conventional temperatures and pressures precludes the occurrence of the usual high temperature problems.

It is anticipated that the use of thermoelectric topping may be an additional step in the economical production of electrical power. A preliminary design consideration shows that a pressurized water reactor design could be easily modified to include a sheath of thermoelectric material between the fuel and the water. Basic efficiency and steam conditions from the Yankee design are used as grounds for system comparison (19).

The efficiency of such a proposed thermoelectric topping design is based on a fuel element design using the same

UO₂ BeO mixture, with dimensions determined by the temperature profile. The coolant outlet temperature is 532°F or 278°C, fuel element centerline temperature is 2760°C and the thermoelectric hot junction is 1072°C and the cold junction 286°C.

$$\eta_{12} = \left(\frac{\Delta T}{T_h}\right) \left[(1 + \bar{T}Z_{12})^{\frac{1}{2}} - 1 \right] / \left[(1 + \bar{T}Z_{12})^{\frac{1}{2}} + T_c/T_h \right] = 12.3\%$$

Thus, based on 545 Mw th reactor core, 59.6 Mw e would be produced by the thermoelectric cells, and about 485 Mw th would be passed on to the steam turbogenerator. Calculations based on the operating data from Yankee, show that an efficiency of 29.1% could be expected for the second cycle using 532°F water at 2000 psia. The steam cycle may yield about 141 Mw e. Thus the total electric output would be 200.6 Mw e giving an over-all plant efficiency of 36.8%.

The available efficiency is of the same order of magnitude as that predicted for the spectral shift reactor or superheater design based on either an integral core or dual reactor. The cost of the superheated reactor power is about 14.7 mills/kwh as opposed to 9.45 mills/kwh for PWR, an increase of 55.5%. Spectral shift costs should be about the same as for the superheater designs.

Another means of evaluating this increase in efficiency is to predict what order of magnitude temperature increase

would be necessary to achieve the same efficiency in a pressurized water cooled reactor. The over-all efficiency of a steam turbine electrical generating system varies with the Carnot efficiency to the first order. An over-all increase of 7.7% must result in a similar increase in the Carnot efficiency.

$$\begin{array}{l} T_h = 551^{\circ}\text{K} \\ T_c = 293^{\circ}\text{K} \end{array} \quad \Delta T = 258^{\circ}\text{K} \quad \eta_c = \frac{T}{T_h} = 56.8\%$$

What T_h is associated with an increase in Carnot efficiency of 7.7%?

$$\eta_c = 54.8\% = \frac{T_h - 293^{\circ}\text{K}}{T_h}, \quad T_h = 644^{\circ}\text{K} \text{ or } 700^{\circ}\text{F}.$$

The pressure of saturated steam at that temperature is 3000 psia, very close to the critical point. This is an indication of the inherent problems at the higher temperature. Most severe will be corrosion problems, and the design of an adequate pressure vessel. The increased cost precludes the development of PWR types to this temperature.

EVALUATION

Thermoelectric materials for which complete experimental data are not known may be evaluated by utilizing theoretical or empirical relations for unknown parameters. The parameter most frequently missing from the literature is the thermal conductivity at high temperature.

Physicists have known for many years that high temperature thermal conductivity is inversely proportional to temperature. Thermal conductivity has two components, one due to the phonon or crystal lattice conduction of thermal energy, and the other due to thermal energy transported by electronic movement through the material.

The electronic contribution to thermal conductivity in semiconductors is expected to be very small due to the low charge carrier density of such materials (36). This electronic component, k_{el} , is shown to be a function of temperature and electrical resistivity.

$$k_{el} = 2(K/e)^2 \sigma T = 1.48 \times 10^{-8} T/\rho \quad (\text{w/cm } ^\circ\text{K})$$

The quantity (K/e) is the Boltzman constant divided by the electronic charge.

The major contribution to thermal conductivity in semiconductors is the lattice or phonon thermal conductivity, k_{ph} . The mechanism which has been accepted as primarily responsible for the lattice thermal resistivity is

phonon-phonon scattering, or the "Umklapp" process (27). This mechanism has been analytically described in several forms (17), and the following equation appears to be most convenient for evaluating the thermal conductivity of materials at high temperatures when experimental values are not available.

$$k_{ph} = B T_m^{1.50} \gamma^{0.66} / M^{1.166} T \quad (\text{w/cm } ^\circ\text{K})$$

The constant, B, has been experimentally evaluated to be 0.06 for semiconductors, giving an expected accuracy for k_{ph} of about one order of magnitude (17). M is the molecular weight in gm, γ is the material density in gm/cm³, and T is the ambient temperature in ^oK.

Thermal conductivity is evaluated, using the above relationships, for a few of the eighteen suggested thermoelectric materials which show high experimental values of (S^2/ρ). In Figures 11, 12, and 13, S, ρ , and k are plotted as a function of temperature for Mg₂Si, Fe₂O₃, and La₂S₃ respectively. The experimental values for these parameters are graphed for CrSi₂ in Figure 14. Reactor calculations have been made, based on CrSi₂ as one of the thermoelectric materials.

The figures of merit for Mg₂Si, Fe₂O₃, and La₂S₃, which are calculated using theoretical values of k, are compared with the figure of merit for CrSi₂ in Figure 15. This

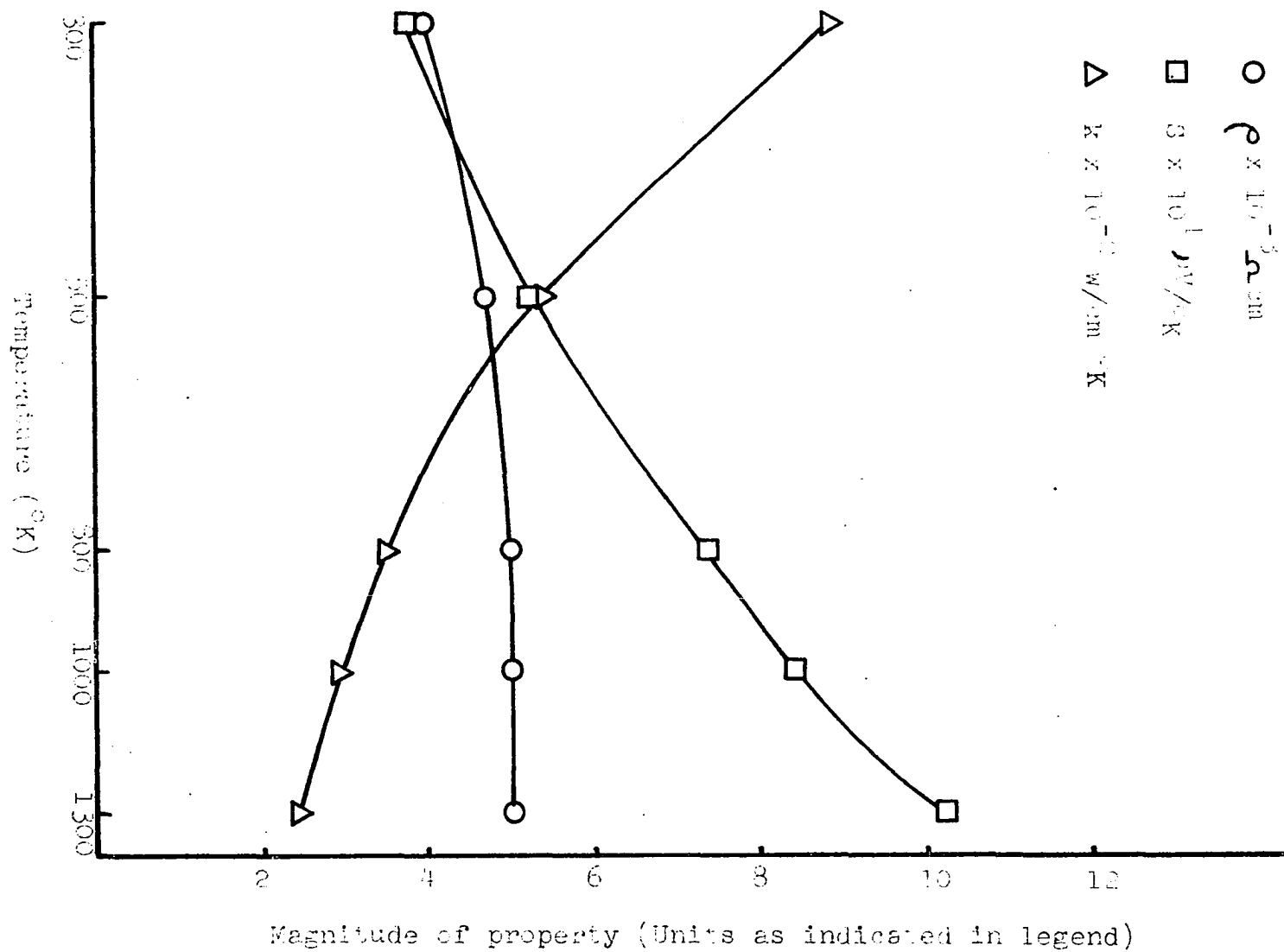
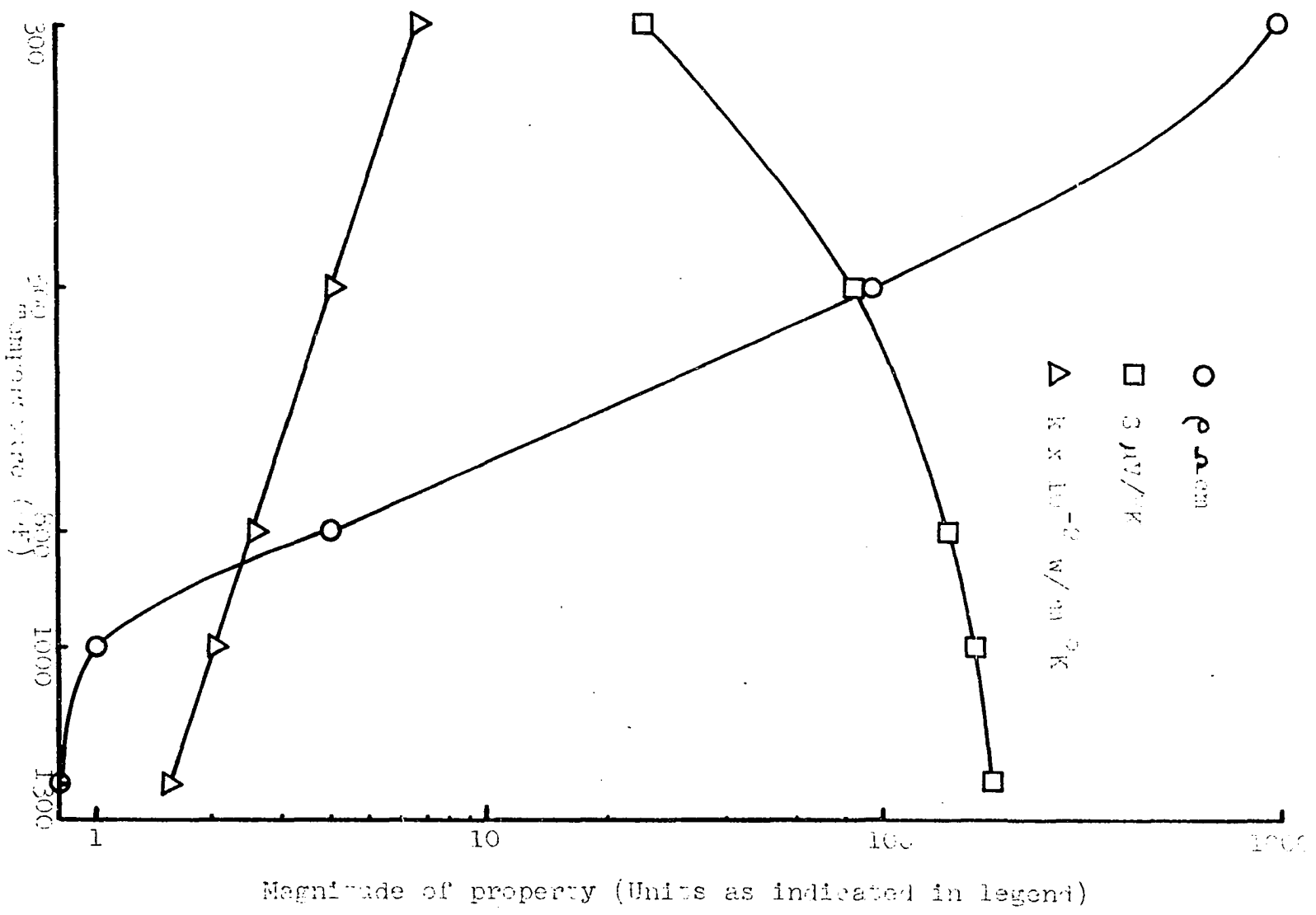
FIGURE 11. Temperature dependence of Fe_2O_3

FIGURE 12. Parameters of FeO_2



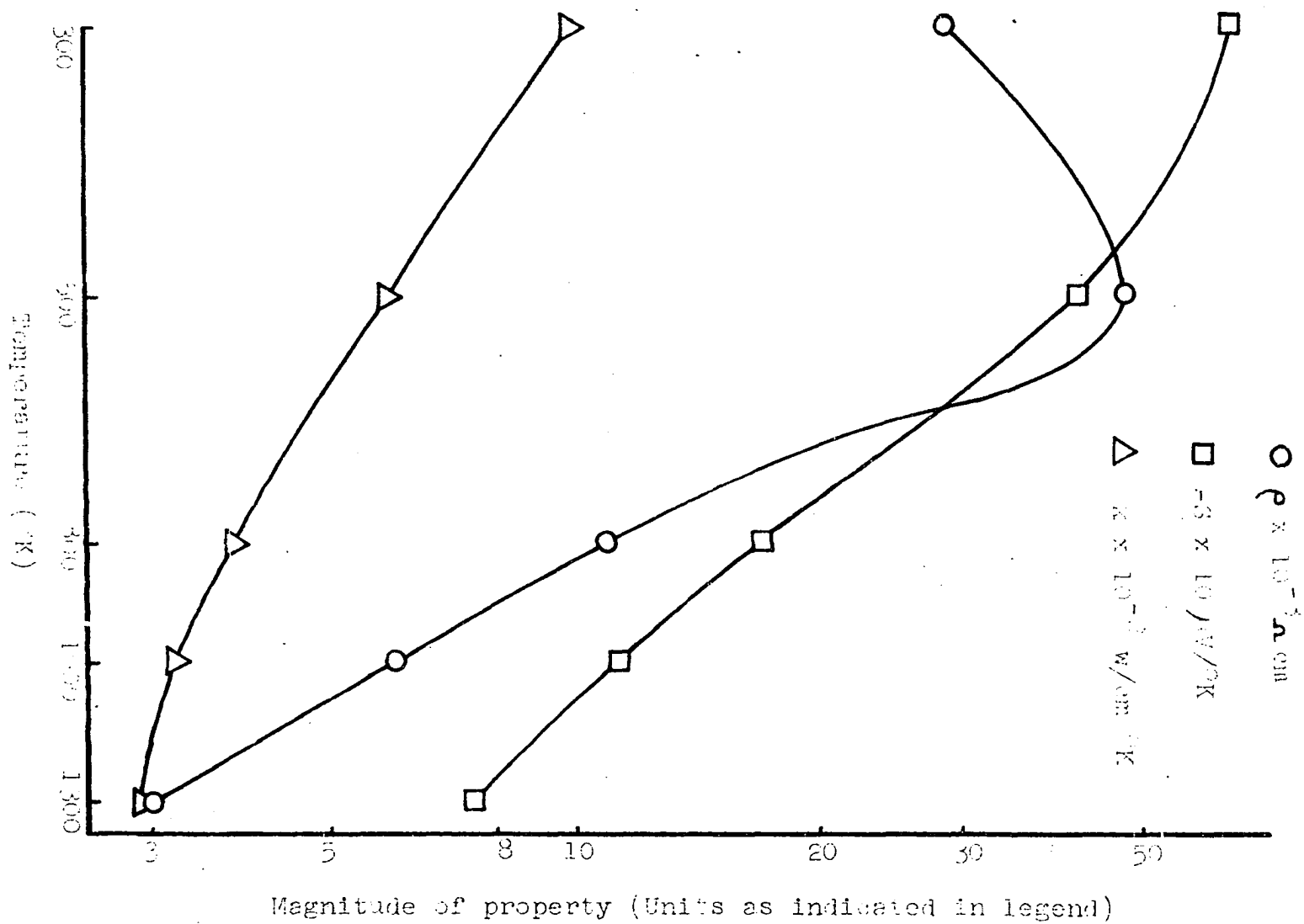


Figure 13. Parameters of MgO.

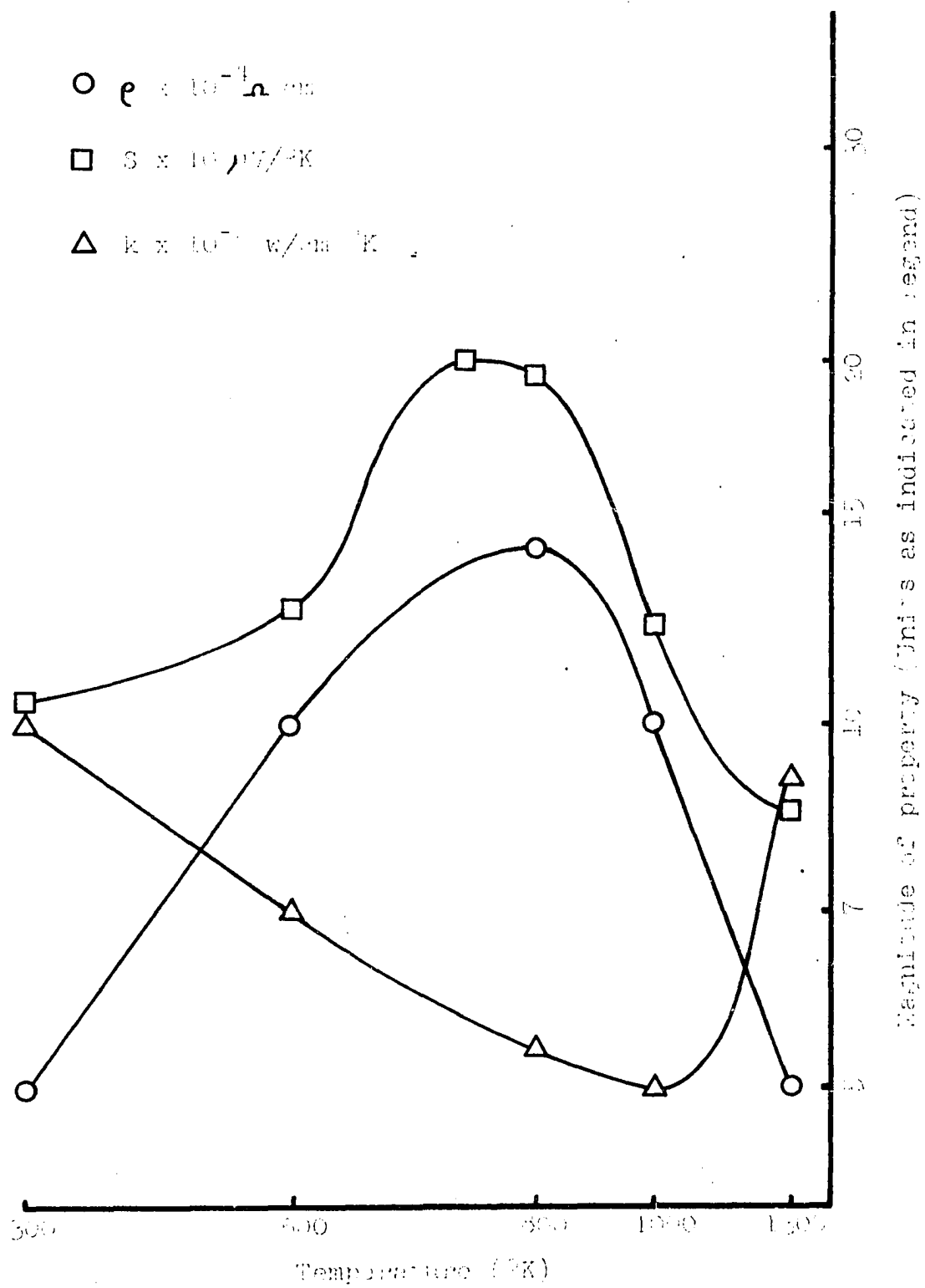


Figure 14. Parameters of CdMg .

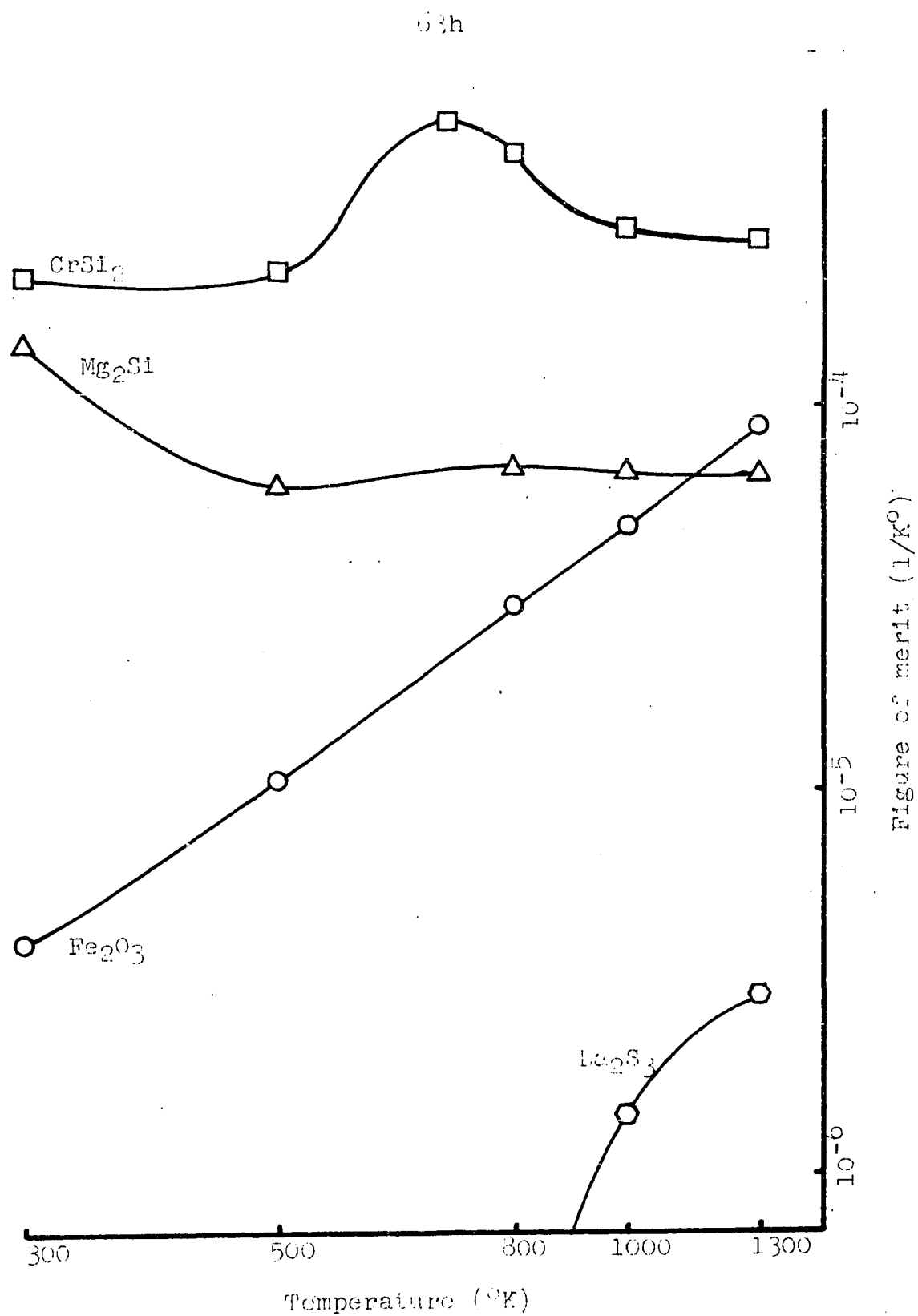


Figure 15. Comparison of figures of merit

comparison indicates that La_2S_3 is not very promising as a thermoelectric material, unless experimental data on its parameters in the range 1300° to 2000°K indicate differently. The high temperature figure of merit for Mg_2Si and Fe_2O_3 is the same order of magnitude as that for CrSi_2 , indicating their suitability as thermoelectric materials. The almost linear rate of increase of Z as a function of temperature for Fe_2O_3 and its high melting temperature, make it very promising as a thermoelectric material. The extrapolated value of Z ($2 \times 10^{-4}/^\circ\text{K}$) for Fe_2O_3 at its melting temperature is competitive with the extrapolated value of Z for CrSi_2 . This, of course, can only be verified experimentally, but it adds to the potential value of the material.

It may be concluded, using the analytical evaluation of Fe_2O_3 , Mg_2Si , and La_2S_3 , that some of the eighteen materials listed as possible high temperature thermoelectric materials have potential value for power conversion at high temperature. Speculations on the usefulness of thermoelectric materials for direct conversion which are made in the literature have included almost every known group of materials. Often this speculation has been virtually groundless, or based on a single parameter such as melting temperature or atomic radius. The analysis in this thesis shows that a prediction of the properties and behavior of high temperature semiconducting materials must be based on at least E_g and T_m . Thermoelectric

behavior, however, must be evaluated by the figure of merit, which is only as reliable as the parameters of the material involved. If two of the three parameters are known experimentally, the third may be calculated from theoretical or empirical relationships to give an order of magnitude value for Z .

This study has shown that a marked continuity in T_m and E_g as a function of the molecular weight, exists for many groups of materials. A group of similar chemical compounds having continuous properties, allows valid interpolation and extrapolation to predict values of E_g and T_m for an unknown compound of the group. This is primarily a tool for directing research and is not reliable enough to be used for the analytical prediction of parameters for use in evaluating Z . The analytical prediction about the usefulness of some of the suggested thermoelectric materials indicates that extensive experimental research is needed in these areas.

High temperature thermoelectric materials are utilized in the design of a nuclear reactor powered direct conversion system. Detailed calculations show that high operating temperature thermoelectric materials are superior to PbTe in the design of a nuclear fuel element for direct energy conversion.

This analysis specifically reveals the desirability of tailoring the thermal conductivity of the nuclear fuel to that of the thermoelectric material surrounding it. This

results in the optimization of the reactor core power density.

Detailed heterogeneous reactor core calculations are performed in this analysis to show that materials other than PbTe may be incorporated into a reactor core in quantities compatible with an integral direct conversion system. This analysis predicts the enrichment of nuclear fuel required for core criticality. The sample calculation outlined in Appendix D allows any material or combination of thermoelectric materials to be analytically evaluated for suitability as in-pile direct conversion materials.

In order to preclude the accumulation of radiation damage, thermoelectric materials should be operated with their cold junction temperature above the annealing temperature of the predominant mechanism in that material. This consideration gives high temperature thermoelectric materials an advantage over conventional ones, in addition to the expected superiority of higher conversion efficiency. It is anticipated that operation at these higher temperatures will result in good system reliability.

CONCLUSIONS

This analysis is a study of high temperature thermoelectric materials in an effort to discover their relative value to the direct conversion of heat to electricity, and to discover their specific applicability to the problem of the conversion of nuclear energy to electricity.

As a result of this study many observations may be made.

1. There are at least eighteen semiconductor materials which can be considered possible thermoelectric materials. Some of their materials parameters have been measured, but not enough data are available to calculate the figure of merit for the material. These materials and their references are listed.

2. Six high temperature thermoelectric materials are verified as suitable for use in the direct conversion of nuclear energy to electricity. Enough experimental data are known for these materials to permit the calculation of the figure of merit for each, and the over-all conversion efficiency of a thermoelectric couple composed of one p and one n type element.

3. Based on the available literature cited, the three most superior high temperature thermoelectric materials, suitable for nuclear power direct conversion, are chromium silicide, germanium silicide, and magnesium antimonide.

4. High temperature thermoelectric materials have at least two distinct advantages over conventional thermoelectric materials. Their conversion efficiency is higher due to the increased Carnot efficiency at higher operating temperatures. Higher operating temperatures insure a wider range for complete annealing of induced radiation damage.

5. The feasibility design of an all thermoelectric conversion system for nuclear fueled specialized power generators shows that this is a competitive if not superior technique. Over-all cell efficiency is 31%, and is expected to be higher than, for example, a two phase mercury turbogenerator.

6. The feasibility design for a central station power reactor core which uses thermoelectric direct conversion as a "topping" technique shows that an increase in over-all efficiency over steam turbogeneration alone is about 7%. This efficiency is equivalent to systems of 55% higher power generating costs.

7. It has been shown in the feasibility designs that in spite of the inclusion of large quantities of thermoelectric materials in the reactor core, considerable freedom still exists for the optimization of a reactor design, based for example on economy, over-all volume, or weight.

8. Criticality studies indicate that even when the

nuclear fuel element is 25% thermoelectric material, and 40% beryllium oxide, the core may be critical for an enrichment of about 4%.

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APPENDIX A

Heat transfer calculations in a slab cell, bonded on two sides by thermoelectric are based on centerline fuel temperature, hot junction and cold junction interface.

$$\begin{aligned} T_o &= 2760^{\circ}\text{C} \\ T_1 &= 1072^{\circ}\text{C} \\ T_2 &= 172^{\circ}\text{C} \end{aligned} \quad \begin{aligned} k_{\text{UO}_2} &= .0176 \text{ w/cm}^{\circ}\text{C} \\ k_{\text{TE}} &= .0192 \text{ w/cm}^{\circ}\text{C} \quad (\text{Appendix C}) \end{aligned}$$

Measured from the centerplane, a is the fuel/thermoelectric interface distance, and b is the thermoelectric/coolant interface.

$$T_o - T_1 = \frac{Qa^2}{2k_{\text{UO}_2}} \quad T_1 - T_2 = Qa\left(\frac{b-a}{k_{\text{TE}}}\right)$$

Assume $(b-a) = .50$ cm, the thickness of the thermoelectric.

$$Qa = \frac{(T_1 - T_2)k_{\text{TE}}}{(b-a)} = 34.6 \text{ w/cm}^2$$

$$a = \frac{2(T_o - T_1)k_{\text{UO}_2}}{Qa} = 1.72 \text{ cm}$$

$$Q = 20.1 \text{ w/cm}^3$$

$$\frac{\text{Volume of T.E.}}{\text{Volume of UO}_2} = \frac{1 \text{ cm}^3}{3.42 \text{ cm}^3} = .292$$

APPENDIX B

Heat transfer calculations in a cylindrical cell, based on the same assumptions as the slab calculation, Appendix A. UO_2 fuel:

$$T_o = 2760^{\circ}C$$

$$T_1 = 1072^{\circ}C$$

$$T_2 = 172^{\circ}C$$

$$k_{UO_2} = .0176 \text{ w/cm}^{\circ}C$$

$$k_{TE} = .0192 \text{ w/cm}^{\circ}C$$

Measured from the fuel element centerline, a is the fuel/thermoelectric interface radius, and b is the thermoelectric/coolant interface radius.

$$T_o - T_1 = \frac{Qa^2}{4k_{UO_2}} \quad T_1 - T_2 = \frac{Qa^2}{2} \left(\frac{1}{k_{TE}} \ln \frac{b}{a} \right)$$

$$\frac{Qa^2}{2} = (T_o - T_1)2k_{UO_2} = 59.4 \text{ w/cm}$$

$$\ln \frac{b}{a} = \frac{(T_1 - T_2)}{\frac{Qa^2}{2}} k_{TE} = 0.291$$

Power density based on 1% enrichment

$$(b - a) = 0.5 \text{ cm}$$

$$a = 1.48 \text{ cm}$$

$$Q = 54.1 \text{ w/cm}^3 \text{ } UO_2$$

$$\frac{\text{Volume of T.E.}}{\text{Volume of } UO_2} = \frac{5.44}{6.90} = .788$$

$$Q = 622 \text{ Kw/KgmU}^{235}$$

APPENDIX C

Calculation of k_{1-2} for high temperature thermoelectrics, based on optimum geometry (5) for the relative volumes of p and n type material. Assume radial dimension is the same for both types, i.e., $l_1 = l_2$.

$$\frac{A_1 l_2}{A_2 l_1} = \left[\frac{\rho_1 k_2}{\rho_2 k_1} \right]^{\frac{1}{2}} \quad \begin{array}{ll} 1 - \text{Mg}_3\text{Sb} & , k_1 = 0.008, \rho_1 = 0.0021 \\ 2 - \text{Ge}_{.3}\text{Si}_{.7} & , k_2 = 0.0345, \rho_2 = 0.1 \\ 3 - \text{Al}_2\text{O}_3 & , k_3 = 0.001 \end{array}$$

Assume insulator area $A_3 = A_1$

$$A_1 = 0.301 A_2 \quad k_{1-2} = \frac{A_1 k_1 + A_2 k_2 + A_3 k_3}{A_1 + A_2 + A_3} = 0.0232 \text{ w/cm}^\circ\text{C}$$

Calculation of k_{2-3} for low temperature thermoelectrics based on similar assumptions

$$\frac{A_4}{A_5} = \left[\frac{\rho_4 k_5}{\rho_5 k_4} \right]^{\frac{1}{2}} \quad \begin{array}{ll} 4 - \text{PbTe}_p & , k_4 = 0.017, \rho_4 = 0.007 \\ 5 - \text{PbTe}_n & , k_5 = 0.0195, \rho_5 = 0.001 \\ 6 - \text{Al}_2\text{O}_3 & , k_6 = 0.001 \end{array}$$

$$A_4 = 2.83 A_5 \quad A_6 = A_5$$

$$k_{2-3} = \frac{A_4 k_4 + A_5 k_5 + A_6 k_6}{A_4 + A_5 + A_6} = 0.0142 \text{ w/cm}^\circ\text{C}$$

Based on these thermal conductivity values, and the hot, intermediate, and cold junction temperatures of $T_1=1345^\circ\text{K}$, $T_2=745^\circ\text{K}$, $T_3=445^\circ\text{K}$, the relative thicknesses of the high and low temperature thermoelectrics are 55% and 45%, hence $k_{1-3} = .0192$ is an approximate total k_{TE} .

APPENDIX D

Cell size optimization:

$$53\% \text{ BeO} \quad 47\% \text{ UO}_2 \quad 3\% \text{ enriched} \quad k = 0.0544 \text{ w/cm}^\circ\text{C}$$

$$Qa^2 = (T_0 - T_1)4k = 240.1 \text{ w/cm}$$

$$T_1 - T_2 = \frac{Qa^2}{2} \left(\frac{1}{k_{TE}} \ln \frac{b}{a} \right) \quad (b-a) = 0.5 \text{ cm} \quad b = 3.73 \text{ cm}$$

$$Q = 23.05 \text{ w/cm}^3 \quad \text{or} \quad 404 \text{ Kw/Kgm U}^{235}$$

$$\text{BeO} - \text{UO}_2 \text{ dispersion: } a = 3.23 \text{ cm} \quad V = 32.75 \text{ cm}^3 \quad \rho = 3.4 \text{ gm/cm}^3$$

Thermoelectric materials:

$$b = 3.73 \text{ cm} \quad V = 10.95 \text{ cm}^3$$

$$\text{"Fuel" region: } R_0 = b = 3.73 \text{ cm} \quad V^0 = 43.70 \text{ cm}^3 \quad \bar{A}^0 = 27.68$$

$$\rho_0 = 3.87 \text{ gn/cm}^3 \quad \Sigma_a^0 = 0.07638 \quad \Sigma_s^0 = 0.4698 \quad D^0 = 0.1482$$

$$L^0 = 1.392 \quad K^0 = 0.7184$$

"Moderator" region: Coolant = H₂O

$$\Sigma_a^m = 0.0221 \quad \Sigma_s^m = 2.67 \quad D^m = 333.3 \quad L^m = 2.714$$

$$a = \left(\frac{K^m R_0}{2} \right)^2 \left(\frac{\rho^0 \bar{A}^m}{\rho^m \bar{A}^0} \right) = 1.188 \quad b = \left(\frac{K^m R_0}{2} \right)^2 \left(\frac{\rho^0 \bar{A}^m}{\rho^m \bar{A}^0} \right) \left(\ln \frac{\rho^0 \bar{A}^0}{\rho^m \bar{A}^m} + 1.5 \right)$$

$$c = \left(\frac{\rho^0 \bar{A}^m}{\rho^m \bar{A}^0} \right) \frac{\Sigma_a^m}{\Sigma_a^0} F - b \quad b = 2.878$$

$$c = -1.633 \quad F = \left(\frac{K^0 R_0}{2} \right) \frac{I_0 (K^0 R_0)}{I_1 (K^0 R_0)} = 1.711$$

Resonance values for cross sections:

$$\Sigma_a^{0'} = 0.0142 \quad K^{0'} = 0.31$$

$$\Sigma_a^{m'} = 0.46 \quad K^{m'} = 0.885$$

$$A = \left(\frac{K^m R_0}{2}\right)^2 \left(\frac{\rho_{A^0}^m}{\rho_{A^0}^m}\right) = 6.854 \quad B = A \left[\ln\left(\frac{\rho_{A^0}^m}{\rho_{A^0}^m}\right) + 1.5 \right] = 16.605$$

$$F = \left(\frac{K^0 R_0}{2}\right) \frac{I_0(K^0 R_0)}{I_1(K^0 R_0)} = 1.158 \quad C = \left(\frac{\rho_{A^0}^m}{\rho_{A^0}^m}\right) \frac{\sum_a^m}{\sum_a^0} F - B = 77.780$$

Maximum K_∞ occurs for $R = N^m/N^0$ when the following equation is true.

$$\frac{c + a \ln R + a}{1 + cR + aR \ln R} - \frac{c + A \ln R + A}{(CR + AR \ln R)^2} = 0$$

$$R \approx .97 = N^m/N^0 \quad N^0 = 3.779 \times 10^{24} \text{ atoms}$$

$$N^m = 3.666 \times 10^{24} \text{ atoms}$$

$$\text{Volume of moderator} = 36.55 \text{ cm}^3 = V^m$$

Part II

Calculate enrichment necessary for criticality. Assume 3% enrichment: $R_0 = 3.73$ $R_1 = 5.05$ $\xi_f^0 = 2.0603$

$$E-1 = \frac{K_1^m (R_1^2 - R_0^2)}{2R_0} \left[\frac{I_0(K^m R_0) K_1(K^m R_1) + K_0(K^m R_0) I_1(K^m R_1)}{I_1(K^m R_1) K_1(K^m R_0) - K_1(K^m R_1) I_1(K^m R_0)} \right]$$

$$E-1 = 0.090$$

$$\frac{1}{F} = 1 + \frac{V^m}{V^0} \frac{\sum_a^m}{\sum_a^0} F + (E-1) = 1.5039 \quad f = 0.665$$

$$\frac{N}{\xi_s} = \frac{N^0 + N^m}{(\xi_s^0 + \xi_s^m)(V^0 + V^m)} = 0.02955 \quad \frac{\xi_s}{N} = 33.84b$$

$$\int_{E_{th}}^{E_0} \sigma_{a,eff} \frac{dE'}{E'} = 17b \quad \bar{\xi} = \frac{\sum_{i=1}^n \xi_{si} f_i}{\sum_{i=1}^n \xi_{si}} = 0.2435$$

$$P_{th} = \exp \left(- \frac{1}{\xi} \frac{N}{\Sigma_s} \int_{E_{th}}^{E_0} \sigma_{a_{eff}} \frac{dE'}{E'} \right) = 0.8845$$

$$\eta = \frac{\nu \Sigma_f}{\Sigma_a} = 1.518 \quad \text{Assume: } \epsilon = 1.03$$

$$K_{\infty} = \eta \epsilon_{pf} = 0.9198$$

Assume 4% enrichment

$$\Sigma_a^0 = 0.09469 \quad \Sigma_f^0 = 2.7470 \quad K^0 = 0.7994$$

$$F = \left(\frac{K^0 R_0}{2} \right) \frac{I_0(K^0 R_0)}{I_1(K^0 R_0)} = 1.8425 \quad E-1 = 0.0900$$

$$\frac{1}{f} = 1 + \frac{V_a^{m,m} \Sigma_a^0}{V^0 \Sigma_a^0} F + (E-1) = 1.449 \quad f = 0.690$$

$$P_{th} = 0.8845 \quad \eta = \frac{\nu \Sigma_f^0}{\Sigma_a^0} = 1.633$$

$$K_{\infty} = \eta \epsilon_{pf} = 1.0267$$

APPENDIX E

| | |
|----------------------------------|--|
| $T_h = 1345^\circ\text{K}$ | |
| Mg_3Sb p type | $\text{Ge}_{.3}\text{Si}_{.7}$ n type |
| $T_2 = 745^\circ\text{K}$ | |
| PbTe p type | PbTe n type |
| $T_c = 445^\circ\text{K}$ | |

| | | | | |
|-------|--------------------------------|-------------|------------------|--------------|
| p_1 | Mg_3Sb | $S = 130$ | $\rho = 0.00211$ | $k = 0.008$ |
| p_2 | PbTe | $S = 300$ | $\rho = 0.007$ | $k = 0.017$ |
| n_1 | $\text{Ge}_{.3}\text{Si}_{.7}$ | $S = -1800$ | $\rho = 0.1$ | $k = 0.0345$ |
| n_2 | PbTe | $S = -290$ | $\rho = 0.001$ | $k = 0.0195$ |

$$\eta = \frac{\eta_c}{\left(\frac{1}{M}\right) + 2\left(\frac{\hat{S}}{S_1}\right) - \eta_c} \quad \eta_c = \frac{(T_h - T_{oc})}{T_h} = 0.669$$

$$S' = \frac{1}{T_h - T_c} \left[S_{p_1}(T_h - T_2) + S_{p_2}(T_2 - T_c) + |S_{n_1}|(T_h - T_2) + |S_{n_2}|(T_2 - T_c) \right]$$

$$= 0.001483$$

$$\hat{S} = |S_{p_1}| + |S_{n_1}| = 0.001930 \quad 2 \frac{\hat{S}}{S_1} = 2.599$$

$$\frac{1}{M} = \frac{4 \left[(\theta_{p_1} k_{p_1} R_{p_1})^{\frac{1}{2}} + (\theta_{n_1} k_{n_1} R_{n_1})^{\frac{1}{2}} \right]^2}{|S'|^2 T_h} = 0.2325$$

Where:

$$\theta_p = \theta_n = \frac{(T_h - T_2)}{(T_h - T_c)} = .666$$

$$k'_{p1} = \frac{k_{p1}}{A_p} = 0.00459 \quad \therefore \eta = 0.309$$

$$R'_p = (\rho_{p1} l_{p1} + \rho_{p2} l_{p2}) = 0.00213$$

$$k'_{n1} = \frac{k_{n1}}{A_n} = 0.00593$$

$$R'_n = (\rho_{n1} l_{n1} + \rho_{n2} l_{n2}) = 0.02822$$

APPENDIX F

$$\begin{aligned}
 T_o &= 2760^{\circ}\text{C} & T_o - T_1 &= \frac{Qa^2}{2k} \\
 T_1 &= 1072^{\circ}\text{C} \\
 T_2 &= 286^{\circ}\text{C} & T_1 - T_2 &= \frac{Qa^2}{2} \left(\frac{1}{k_{TE}} \ln \frac{b}{a} \right) \\
 T_f &= 278^{\circ}\text{C}
 \end{aligned}$$

$$\begin{aligned}
 k_{\substack{53\% \text{ BeO} \\ 47\% \text{ UO}_2}} &= .0544 \text{ w/cm}^{\circ}\text{C} & Qa^2 &= 183.5
 \end{aligned}$$

$$k_{TE} = 0.0232 \quad (b-a) = 0.5 \text{ cm} \quad ; \quad a = 2.275 \text{ cm}$$

$$Q = 35.5 \text{ w/cm}^3$$

Based on 3% enrichment as is Yankee

$$Q = 623 \text{ Kw/Kgm U}^{235}$$